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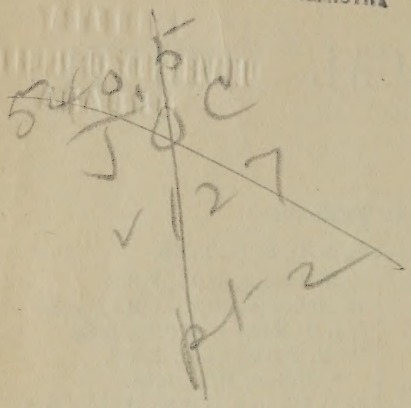
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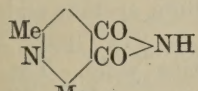


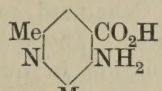
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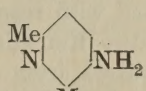
CC.—*Synthetical Experiments in the Naphthyridine Groups.*

By JOHN MASSON GULLAND and ROBERT ROBINSON.

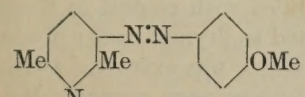
THE sodamide method of Tschitschibabin (*J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1216; 1915, **47**, 835) has rendered many α- and γ-aminopyridine derivatives readily accessible, but it is still difficult to obtain β-aminopyridines in quantity. We have utilised the fact that 2 : 6-dimethylcinchomeronic acid is easily prepared (Mumm and Hüneke, *Ber.*, 1917, **50**, 1568) in devising a method of preparation of 3-amino-2 : 6-lutidine (III). 2 : 6-Dimethylcinchomeronimide (I), obtained from the acid by heating with carbamide (compare Herzog, *Z. angew. Chem.*, 1919, **32**, 301; Lawson, Perkin, and Robinson, J., 1924, **125**, 634), is converted by potassium hypobromite and potassium hydroxide into a salt of 3-amino-2 : 6-dimethyl*iso*nicotinic acid (II). This acid yields the aminolutidine on distillation with soda-lime. The product is quite different

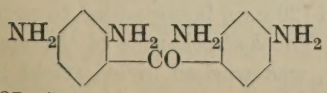

(I.)

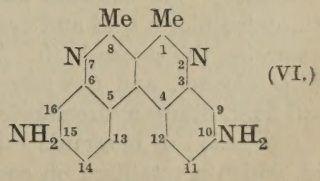

(II.)


(III.)

from 4-amino-2 : 6-lutidine (Marckwald, *Ber.*, 1894, **27**, 1325), and this fact establishes the constitution of the new base. We have made many fruitless attempts to convert this aminolutidine into 1 : 7-naphthyridine derivatives, for example, by condensation with acetylacetone and by application of the Doebner-Miller synthesis. The reactivity of the nucleus appears to be feeble. The diazonium salt derived normally from the base couples with phenol with formation of lutidineazophenol, the *O*-methyl ether (IV) of which was examined by the method of Jacobson for the semidine transformation on reduction. No evidence of this was obtained, and as regards the benzidine transformation, Friedl (*Monatsh.*, 1913, **34**, 765) has prepared 3-hydrazopyridine, but makes no mention of a molecular rearrangement of this substance. Intramolecular changes of these types are clearly not facile in the pyridine series.

(IV.) 

(V.) 


(VI.)

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The copyrine synthesis from derivatives of *oo*-diaminobenzophenone and 1 : 3-diketones described by Lawson, Perkin, and Robinson (*loc. cit.*) involves a very satisfactory reaction from the point of view of yield and convenience, but the number of available diaminobenzophenones is limited. We have now obtained 2 : 4 : 2′ : 4′-*tetra-aminobenzophenone* (V), and from it, by condensation with acetylacetone, a *diaminodimethyldibenzocopyrine* (VI).

Further brief indications of synthetical schemes will be found in the experimental section.

Experimental.

2 : 6-*Dimethylcinchomeronimide* (I).—In the preparation of 2 : 6-dimethylcinchomeronic acid (Mumm and Hüneke, *loc. cit.*) the isolation of the ester was found to be unnecessary. The product of the condensation of ethyl acetylpyruvate (83 g.) with ethyl β-aminocrotonate (69·3 g.) in ether (40 c.c.) was, after 15 hours, hydrolysed with potassium hydroxide (25 g.) dissolved in 70% alcohol (150 c.c.). Following steam distillation, the liquid was acidified with respect to Congo-red, and sodium acetate added to neutralise the mineral acid. The acid, m. p. 274° (pure 275°), crystallised from the solution in quantitative yield. The conversion into the *imide* by heating the ammonium salt at 230°, as described by Mumm and Hüneke, is troublesome, and the following process is far more convenient. The acid (10 g.) and carbamide (5 g.) were heated together with stirring at 225° until ammonia was no longer evolved (about 5 minutes), then at 230° for a few moments, and the mass was cooled and extracted with alcohol. The substance, m. p. 230° (Mumm and Hüneke give m. p. 230°), crystallises from the solution in yellow needles (yield 81%).

3-*Amino*-2 : 6-*dimethylisonicotinic Acid* (II). (Compare Gabriel and Colman, *Ber.*, 1902, **35**, 2832, for the preparation of 3-amino-*iso*nicotinic acid from cinchomeronimide).—Finely-powdered 2 : 6-dimethylcinchomeronimide (20 g.) dissolved when it was gradually added to a well-stirred, ice-cold solution of potassium hypobromite prepared from bromine (18·2 g.) and 10% aqueous potassium hydroxide (300 c.c.). After 2 hours, 10% potassium hydroxide (160 c.c.) was added and the mixture heated for 10 minutes on the steam-bath. The solution was acidified with respect to Congo-red with hydrochloric acid and evaporated to dryness under diminished pressure on the steam-bath. The residue was extracted twice with boiling alcohol, and the filtered solutions were concentrated to a small bulk, dilute hydrochloric acid (20 c.c.) being added to prevent the separation of inorganic salts. The *hydrochloride* of the amino-acid, which crystallised on cooling, was washed, dried (yield 16 g.

or 60%), and recrystallised from dilute hydrochloric acid, separating in slender, pale yellow needles, decomp. 248° (Found in material dried over sulphuric acid: Cl, 14·9; loss at 110°, 8·4; loss at 130°, 15·2. $C_8H_{11}O_2N_2Cl,2H_2O$ requires Cl, 14·9; $1H_2O$, 7·6; $2H_2O$, 15·1%). The long, yellow needles which separate from alcohol have m. p. 253—255° with previous slight darkening. This salt is readily soluble in water and sparingly soluble in dilute hydrochloric acid. The amino-group can be diazotised and coupling with β-naphthol produces a red azo-compound.

Sodium acetate was added to a concentrated aqueous solution of the hydrochloride, and the pale yellow, oblique-ended prisms of the *acid* which slowly separated were washed, and dried over sulphuric acid (Found: loss at 110°, 5·1; in material dried at 110°, C, 57·9; H, 6·1. $C_8H_{10}O_2N_2,0{\cdot}5H_2O$ requires H_2O, 4·9. $C_8H_{10}O_2N_2$ requires C, 57·8; H, 6·0%). The acid is sparingly soluble in neutral organic solvents, more readily soluble in water, and easily soluble in alcohol; it melts at 295° after darkening at 285°. The *copper* salt occurs in yellow, prismatic needles, moderately soluble in water, and the *lead* salt in colourless, quadrilateral or hexagonal prisms which do not melt at 315°.

3-*Amino*-2 : 6-*lutidine* (III).—A mixture of the hydrochloride of aminodimethyl*iso*nicotinic acid (15 g.) with powdered soda-lime (5 parts) was strongly heated in a combustion tube in a stream of hydrogen. The distillate, which solidified (6·4 g.), crystallised from benzene in colourless needles, m. p. 122°, and from water in needles which melted indistinctly between 70° and 75° and lost 14·4% on drying over potassium hydroxide in a vacuum; they then melted at 122° (Found: C, 68·7; H, 8·4; N, 22·9. $C_7H_{10}N_2$ requires C, 68·8; H, 8·2; N, 22·9% and $C_7H_{10}N_2,H_2O$ requires H_2O, 14·7%). This strong base has a characteristic odour and is readily soluble in most organic solvents, although somewhat sparingly soluble in ether. The *hydrochloride* is very readily soluble in water and separates from alcohol in flat needles, m. p. 235°.

3-p-*Hydroxybenzeneazo*-2 : 6-*lutidine* (corresponding with IV).—3-Aminolutidine (4·2 g.) was diazotised below 2° in hydrochloric acid (13·7 c.c.; *d* 1·16) and water (80 c.c.) with sodium nitrite (3·6 g.) in water (50 c.c.). The diazo-solution was slowly added to a cold, agitated solution of phenol (3·2 g.) and sodium hydroxide (6·9 g.) in water (100 c.c.), and, after 5 minutes, the dark red solution was saturated with carbon dioxide. The orange-brown precipitate, after being washed and dried (yield 6·7 g. or 86%), crystallised from toluene in flat, orange needles, m. p. 240° (decomp.) (Found in material dried at 110°: C, 68·9; H, 5·9; N, 18·6. $C_{13}H_{13}ON_3$ requires C, 68·7; H, 5·7; N, 18·9%). The substance is sparingly

soluble in ether, benzene, or chloroform, and is moderately readily soluble in alcohol, acetone, or ethyl acetate. The solutions in concentrated sulphuric and hydrochloric acids are bright red and the *hydrochloride* crystallises from dilute hydrochloric acid in orange-yellow needles, m. p. 239—240° (decomp.) (depressed by admixture with the base). In caustic alkalis, an orange-red solution is obtained, but the compound is less readily soluble in aqueous ammonia than benzeneazophenol.

The *methyl* ether (IV), which could not be obtained by the action of methyl sulphate on the phenol, since methylation of the tertiary nitrogen atom ensued, was prepared by Pyman's method (J., 1918, **113**, 227) for the *O*-methylation of phenolic bases; the conversion of benzeneazophenol into benzeneazoanisole by this process was found to be 75%. The lutidineazophenol (2 g.) and sodium methyl sulphate (3·6 g.; 3 mols.) were added to a solution of sodium *iso*amyloxide (from 0·2 g. of sodium) in *iso*amyl alcohol (20 c.c.), and the mixture was boiled under reflux for 2 hours, the colour changing from red to dark brown. Ether and dilute sodium hydroxide solution were added to the cold mixture, and the ethereal layer was washed with dilute alkali and water, filtered, and the solvent removed by distillation and steam distillation. The residue crystallised on cooling (yield 1·86 g. or 87·7%); 0·25 g. of unchanged phenol was recovered. *Lutidineazoanisole* is rather readily soluble in organic solvents and crystallises from light petroleum in elongated, diamond-shaped, red plates, often forming radiating clusters; it melts at 81—82° and solidifies to a yellow mass on cooling. When the bright red crystals were collected, they became yellow in places, but the change did not progress on keeping (Found: C, 69·6, 69·4; H, 6·2, 6·2. $C_{14}H_{15}ON_3$ requires C, 69·7; H, 6·2%). The *hydrochloride*, orange needles, sparingly soluble in dilute hydrochloric acid, melts to a paste at 112°, but, after drying at 100°, has m. p. 183—185° (decomp.). The semidine transformation was attempted by treatment of the ether both with acid reducing agents, such as alcoholic stannous chloride and hydrochloric acid, and with neutral reducing agents, such as aluminium–mercury and alcohol, and hydrogen in presence of palladium, followed by treatment with acids. The products gave no trace of triazole derivatives on treatment with nitrous acid. The failure of the semidine rearrangement also involved the breakdown of an otherwise feasible synthesis of harmine.

Derivatives of 3-*Amino*-2-*methylcinchoninic Acid*.—The object in view in making the experiments described below was the conversion of the accessible 3-amino-2-methylcinchoninic acid (Lawson, Perkin, and Robinson, *loc. cit.*) into a 1 : 7-naphthyridine derivative

by applying the Camps synthesis of 2 : 4-dihydroxyquinoline from anthranilic acid (*Arch. Pharm.*, 1899, **237**, 659). The attempt was abandoned on account of the difficulties encountered, and indicated in the sequel, but also because Seide (*Ber.*, 1924, **57**, 1806) failed to obtain a naphthyridine derivative in a similar manner from 2-aminonicotinic acid.

Methyl 3-*Amino*-2-*methylcinchoninate*.—The acid is not esterified when its solution in dry methyl alcohol (25 g. in 500 c.c.) is saturated with hydrogen chloride and heated under reflux for 3·5 hours. This phenomenon is not abnormal, since the conditions for the exercise of powerful steric hindrance are present, whilst, in addition, the basic character of the substance operates against the exhibition of oxonium character by the oxygen atoms of the carboxyl group.

A mixture of the acid (10 g.), sulphuric acid (10 c.c.), and methyl alcohol (100 c.c.) was boiled under reflux for 7 hours. Barely 1 g. of the *ester* was ultimately isolated as a viscous, yellow oil which soon solidified; it crystallised from light petroleum (b. p. 60—80°) in canary-yellow needles, m. p. 83—84° (Found : C, 66·4; H, 5·6. $C_{12}H_{12}O_2N_2$ requires C, 66·7; H, 5·6%). The substance exhibits brilliant blue fluorescence in ethereal solution, and is readily soluble in dilute hydrochloric acid and most organic solvents. The *acetyl* derivative was apparently not produced by the action of boiling acetic anhydride alone, but when the ester was boiled with an excess of acetic anhydride and fused sodium acetate for 10 minutes a substance was isolated in about 35% yield, which crystallised from benzene–light petroleum in pale yellow needles, m. p. 169°. This is doubtless *methyl* 3-*acetylamino*-2-*methylcinchoninate*, but the method of preparation is very unsatisfactory and attempts, unfortunately fruitless, were made to reverse the order of the operations. 3-*Acetylamino*-2-*methylcinchoninic acid*. A mixture of amino-methylcinchoninic acid (10 g.), fused sodium acetate (10 g.), and acetic anhydride (30 c.c.) was gently heated over a free flame until a vigorous reaction set in and the yellow colour disappeared. After being heated to incipient ebullition for a minute, the product was cooled, decomposed with water, and the precipitate collected and dried (10 g.). The material was a mixture, and an acidic fraction was separated from a neutral fraction (A) by means of dilute aqueous sodium carbonate. The acid precipitated from the filtered alkaline solution was at first gelatinous, but became crystalline when the mixture was heated on the steam-bath for about 10 minutes. The substance crystallises from much hot water in small, colourless needles which, after drying in a vacuum, lose 10·3% at 100° and then have m. p. 286° (Found in material dried at 100° : C, 64·2; H, 4·9. $C_{13}H_{12}O_3N_2,1{\cdot}5H_2O$ requires H_2O, 9·6% and $C_{13}H_{12}O_3N_2$

requires C, 63·9; H, 4·9%). This compound is sparingly soluble in most organic solvents, but dissolves in dilute hydrochloric acid at about 40° and separates again on cooling. The acetyl group was not removed when a solution of the substance in dilute aqueous sodium hydroxide was boiled for 4 hours; a sodium salt separated in silky needles from the cooled solution and by treatment with dilute acetic acid gave the unchanged acid, m. p. 286°.

A curious result followed an attempt to esterify the acid. A mixture of 3-acetylamino-2-methylcinchoninic acid (2 g.), sulphuric acid (3 c.c.), and methyl alcohol (20 c.c.) was boiled under reflux for 3·5 hours. After distillation of half the methyl alcohol, the mixture was added to water and ammonia and extracted with ether, which removed nothing. The ammoniacal solution was then acidified with hydrochloric acid and, on keeping, 1·9 g. of a yellow substance separated which crystallised from water in feathery, yellow needles, m. p. 217° (decomp.) [Found: loss at 100°, 14·3; in material dried at 100°, C, 64·8; H, 5·1. $C_{24}H_{22}O_5N_4(2C_{11}H_{10}O_2N_2 + C_2H_4O_2 - H_2O)$ requires C, 64·6; H, 4·9% and $C_{24}H_{22}O_5N_4,4H_2O$ requires H_2O, 13·9%). When the acetylamino-acid was boiled with concentrated hydrochloric acid it was quickly converted into an acid, devoid of basic properties, which, crystallised from dilute hydrochloric acid and then from alcohol, formed bright yellow needles, m. p. 234—235° (Found in material dried in a vacuum: loss at 100°, 5·6; in material dried at 100°, C, 63·1, 63·4; H, 5·5, 5·6; N, 12·8%). Both substances, m. p. 217° and m. p. 234—235°, are acids which are readily soluble in aqueous sodium carbonate, and the latter was shown to be unaffected by boiling dilute aqueous sodium carbonate in ½ hour. We have not reached any definite conclusion as to the nature of these substances.

Anhydro-3-acetylamino-2-methylcinchoninic Acid.—The material (A) obtained in the course of the acetylation of aminomethylcinchoninic acid crystallised from alcohol or benzene in colourless needles, m. p. 199—200° (Found: C, 69·1; H, 4·6; N, 12·2. $C_{13}H_{10}O_2N_2$ requires C, 69·0; H, 4·4; N, 12·4%). On boiling with water, the substance is slowly hydrated, but more rapidly in presence of sodium hydroxide, with the formation of 3-acetylamino-2-methylcinchoninic acid, m. p. 286°. The substance resembles acetylanthranil (compare Schroeter and Eisleb, *Annalen*, 1909, **367**, 124), and its constitution is probably analogous (O instead of NPh) to that of the pyrimidine derivative described below.

1-*Keto*-2-*phenyl*-3 : 5-*dimethyl*-1 : 2-*dihydro*-2 : 4 : 6-*naphtha*iso-*triazine*, $C_9H_4MeN<\begin{matrix}CO\cdot NPh\\ N=CMe\end{matrix}$.—A mixture of anhydro-3-acetylamino-2-methylcinchoninic acid (0·7 g.) and aniline (2 c.c.) was

boiled for 2 minutes and cooled, and the product was washed with alcohol and crystallised from much alcohol, separating in yellow needles, m. p. 235° (Found : C, 75·6; H, 5·3. $C_{19}H_{15}ON_3$ requires C, 75·7; H, 5·0%). This sparingly soluble substance is a weak base and is precipitated unchanged on addition of water to its solution in concentrated hydrochloric acid.

2 : 4 : 2′ : 4′-*Tetra-aminobenzophenone* (V).—Schöpff's method of tetra-nitration of diphenylmethane (*Ber.*, 1894, **27**, 2318) resulted in inferior yields, and the following method effected a considerable improvement. Molten diphenylmethane (53 g.) was added drop by drop to a stirred solution of potassium nitrate (128 g.) in sulphuric acid (360 g.) maintained below 25°. An equal quantity of potassium nitrate was then introduced and the mixture frequently shaken and heated on the steam-bath for 30 minutes. The isolation was by the method of Schöpff, and the yield 70%. The oxidation of tetranitrodiphenylmethane with chromic and acetic acids as described by Städel (*Annalen*, 1883, **218**, 341) proved a most unsatisfactory process and, after numerous trials, we finally adopted the following conditions. Tetranitrodiphenylmethane (10 g.) was dissolved in concentrated sulphuric acid (90 g.) and water (10 g.), and a concentrated aqueous solution of chromic acid (5·8 g.) added with vigorous agitation, the temperature being maintained below 40°. The mixture was finally heated for an hour on the steam-bath, added to water, and the precipitate collected and dried (7·5 g. or 72%). A specimen crystallised from acetic acid melted at 224—225° and for ordinary purposes the crude product can be satisfactorily purified by extraction with hot ethyl acetate. A good criterion of purity is the absence of the blue coloration with alcoholic potassium hydroxide which is so characteristic of tetranitrodiphenylmethane.

The tetranitrobenzophenone (10 g.) was suspended in a mechanically stirred mixture of acetic acid (100 c.c.) and concentrated hydrochloric acid (65 c.c.), and granulated tin (45 g.) gradually added. After about 20 hours, the liquid contained no solid nitrocompound in suspension and gave a clear solution with water. Sufficient water to dissolve the tin salt was added, and the filtered solution rendered strongly alkaline by the addition of sodium hydroxide. After a few hours, the black sludge and yellow needles were collected, dried, and extracted several times with hot alcohol. Dull, yellow prisms (3 g.) separated on cooling the concentrated extracts; the base, recrystallised from alcohol, had m. p. 202° (Found : C, 64·5; H, 6·0; N, 23·2. $C_{13}H_{14}ON_4$ requires C, 64·5; H, 5·8; N, 23·1%). Tetra-aminobenzophenone is readily soluble in acetone, ethyl acetate, or methyl alcohol, sparingly soluble in

benzene or chloroform, and very sparingly soluble in ether. Just above its m. p. the substance evolves ammonia; the residue dissolves in dilute hydrochloric acid, the yellow solution exhibiting bluish-green fluorescence. This behaviour indicates the formation of diaminoacridone. On treatment of an acid solution with sodium nitrite, a brown precipitate is thrown down and the solution contains a diazonium salt.

10 : 15-*Diamino*-1 : 8-*dimethyldibenzocopyrine* (VI). — Concentrated hydrochloric acid (5 c.c.) was added to a mixture of 2 : 4 : 2′ : 4′-tetra-aminobenzophenone (1 g.), acetylacetone (1 g.), and water (25 c.c.), and the whole gently heated. In about ½ minute orange crystals separated and the mixture was then boiled for a minute and cooled. The crystals were collected, washed with alcohol, and dried in a vacuum (Found : Cl, 26·6. $C_{18}H_{16}N_4$,3HCl requires Cl, 26·7%). This *hydrochloride* occurs in orange-red, rectangular plates, which decompose without melting at 310°. It crystallises in beautiful leaflets when hydrochloric acid is added to an aqueous solution. The yield in the preparation is almost quantitative if account be taken of the small amount of base recoverable from the original filtrate. In order to obtain the free base, the salt was dissolved in boiling dilute acetic acid and potassium hydroxide added until crystals began to separate. The heating was then discontinued and the remainder of the base precipitated by the further addition of potassium hydroxide. The substance was collected, washed, dried, and dissolved in a large volume of hot alcohol (charcoal). The filtered solution was concentrated by distillation and, at a certain stage, pale brown cubes were deposited from the hot solution (Found : C, 75·2; H, 5·6; N, 19·2. $C_{18}H_{16}N_4$ requires C, 75·0; H, 5·6; N, 19·4%). The substance is sparingly soluble in most organic solvents and its alcoholic solution exhibits a weak green fluorescence. It begins to decompose at about 305°, but does not melt at 340°. The base can be normally tetrazotised and coupled with β-naphthol to produce a crimson azo-compound.

An attempt to shorten the preparation was made, the product of reduction of tetranitrobenzophenone (1 mol.) being treated with zinc to eliminate tin and then with acetylacetone (3 mols.) on the steam-bath. After the red precipitate had been treated with successive quantities of cold alcohol, the residue consisted of the above-mentioned trihydrochloride. The alcoholic filtrates were evaporated to dryness; the residue crystallised from dilute hydrochloric acid in dark red needles which, air-dried, lost 19·6% at 130°, leaving a purplish-brown mass with a green reflex. This salt exhibits a most brilliant green fluorescence in solution and contains a diazo-

tisable amino-group. The amount of material at our disposal did not permit of further investigation.

Benzoylveratroylmethane, $PhCO{\cdot}CH_2{\cdot}CO{\cdot}C_6H_3(OMe)_2$. — Ethyl veratrate (10·5 g.) and acetophenone (7·5 g.) were condensed together by means of granulated sodium (2·3 g.) under dry ether (50 c.c.), and the diketone was isolated as the *copper* salt (5 g.) in the usual manner. This substance crystallised from benzene in pale green leaflets, m. p. 250° (Found: Cu, 10·1. $C_{34}H_{30}O_8Cu$ requires Cu, 10·1%). The *benzoylveratroylmethane* obtained by its decomposition with dilute sulphuric acid in presence of ether crystallised from methyl alcohol in pale yellow plates, m. p. 67°, and was readily soluble in most organic solvents (Found: C, 71·7; H, 5·6. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·6%). An alcoholic solution is coloured greenish-brown on the addition of ferric chloride.

Ethyl Benzoylveratroylacetate, $(MeO)_2C_6H_3{\cdot}CO{\cdot}CH(CO_2Et){\cdot}COPh$. —As the yield of benzoylveratroylmethane was rather poor in the direct process, this ester was prepared, but it could not be hydrolysed so as to yield the desired product.

Solutions of sodium ethoxide (from 8·7 g. of sodium) in alcohol (147 c.c.) and of veratroyl chloride (39·5 g.) in benzene (500 c.c.) were prepared. Half the sodium ethoxide solution was added to ethyl benzoylacetate (37·8 g.), and the mixture stirred and cooled to 0°. Half the veratroyl chloride solution was added during 15 minutes, and the mixture allowed to remain for 30 minutes. The cycle of operations was repeated several times, on each occasion one-half of the volume of the solution which remained being added. After 12 hours, the dense, yellow precipitate of crude sodium salt was collected, washed with benzene, dried in the air, and decomposed in aqueous solution with 2*N*-hydrochloric acid. The bulky, white precipitate of the ester was taken up with ether and the extract rapidly dried and concentrated, when, on standing, most of the product separated in colourless nodules. The substance was recrystallised by addition of light petroleum to a benzene solution (at about 50°), the long, slender needles obtained having m. p. 125—126° (Found: C, 68·9; H, 5·8. $C_{20}H_{20}O_6$ requires C, 68·9; H, 5·7%). Ferric chloride added to an alcoholic solution developed a red coloration. When the ester (15 g.) was boiled with aqueous ammonia (10·8 c.c.; *d* 0·880) in water (100 c.c.) for 5 minutes, the chief products were benzamide and ethyl veratroylacetate; veratramide, veratric acid, and acetophenone were also formed. Benzoic acid and acetoveratrone did not appear to be among the products of hydrolysis.

2 : 4-*Dinitro*-3′ : 4′-*methylenedioxystilbene*.*—We have prepared

* This work on some derivatives of stilbene was carried out in collaboration with William Stafford.

some stilbene derivatives in order to attempt to obtain 2 : 6-naphthyridine derivatives by the dehydration of *oo*-diacylaminostilbenes.

A molten mixture of piperonal (23 g.), 2 : 4-dinitrotoluene (27 g.), and piperidine (30 drops) was heated on the steam-bath for 3 hours, when the mass became solid. The very sparingly soluble product crystallised from acetic acid in bright salmon prisms, m. p. 180° (Found : C, 57·3; H, 3·2. $C_{15}H_{10}O_6N_2$ requires C, 57·3; H, 3·2%).

4-*Nitro*-2-*amino*-3′ : 4′-*methylenedioxystilbene*.—A cooled solution of dinitromethylenedioxystilbene (20 g.) in acetic acid (300 c.c.) was mixed with a solution of crystallised stannous chloride (40 g.) in acetic acid containing hydrogen chloride and stirred in the cold for 6 hours. The orange-yellow tin salt obtained was digested with water, and from the free, red amino-derivative produced the hydrochloride was prepared in alcoholic solution, and decomposed by water. The base crystallised from alcohol in dark red prisms, m. p. 213° (Found : C, 63·3; H, 4·4. $C_{15}H_{12}O_4N_2$ requires C, 63·4; H, 4·2%). Its constitution may be inferred from the results of Thiele and Escales (*Ber.*, 1901, **34**, 2842) relating to the semi-reduction of 2 : 4-dinitrostilbene combined with the fact that ammonia and hydrogen sulphide reduced dinitromethylenedioxystilbene to a quite different isomeric base.

2 : 4-*Dinitro*-2′ : 3′-*dimethoxystilbene* was prepared from 2 : 4-dinitrotoluene (18 g.), 2 : 3-dimethoxybenzaldehyde (17 g.), and piperidine (20 drops) as described above. It crystallised from acetic acid in bright yellow prisms, m. p. 165° (yield 31 g.; 94%) (Found : C, 57·9; H, 4·4. $C_{16}H_{14}O_6N_2$ requires C, 58·2; H, 4·3%).

2-*Nitro*-4-*amino*-2′ : 3′-*dimethoxystilbene*.—The conditions for the satisfactory preparation of 2-nitro-4-aminostilbene itself have been studied and the following method gives good results (compare Thiele and Escales, *loc. cit.*). Hydrogen sulphide was led for 3 hours through a gently refluxing mixture of dinitrostilbene (20 g.), alcohol (250 c.c.), and aqueous ammonia (30 c.c.; *d* 0·880). The cooled solution was filtered, and the hydrochloride precipitated with hydrogen chloride; the base obtained from the salt separated from alcohol in red crystals, m. p. 110°.

Nitrostilbenediazonium hydrogen sulphate is readily isolable in the crystalline condition and on decomposition with aqueous potassium iodide gives 4-*iodo*-2-*nitrostilbene*, bright yellow crystals, m. p. 105°. A similar reduction process was applied to dinitro-2′ : 3′-dimethoxystilbene and orange-red needles, m. p. 121—122°, were obtained (Found : C, 63·6; H, 5·2. $C_{16}H_{16}O_4N_2$ requires C, 64·0; H, 5·3%).

2 : 4-*Dinitro*-3′ : 4′-*dimethoxystilbene*, prepared from veratraldehyde and 2 : 4-dinitrotoluene, crystallises from acetic acid in

stout, maroon prisms, m. p. 143°, sparingly soluble in alcohol (Found : C, 58·0; H, 4·4. $C_{18}H_{14}O_6N_2$ requires C, 58·2; H, 4·3%). When triturated with acetic acid (35 c.c.) and nitric acid (25 c.c.; *d* 1·42), the substance (19 g.) became yellow; the product crystallised from acetic acid in short, yellow prisms, m. p. 192° (Found : N, 11·3. $C_{16}H_{13}O_8N_3$ requires N, 11·2%).

2 : 4 : 6′-*Trinitro*-3′ : 4′-*dimethoxystilbene* is readily soluble in acetone, but sparingly soluble in most other organic solvents.

2 : 4-*Dinitro*-2′-*hydroxystilbene* is obtained in poor yield from 2 : 4-dinitrotoluene and salicylaldehyde in presence of piperidine. It crystallises from ethyl alcohol in light brown, irregular granules, m. p. 179—181° (Found : C, 58·6; H, 3·6. $C_{14}H_{10}O_5N_2$ requires C, 58·7; H, 3·5%), is readily soluble in most organic solvents, develops no coloration with alcoholic ferric chloride, and dissolves in aqueous sodium hydroxide to a red solution.

2 : 4-*Dinitro*-3′-*methoxy*-4′-*hydroxystilbene*, produced (yield 67%) by condensation of 2 : 4-dinitrotoluene and vanillin in presence of piperidine, crystallises from acetic acid in stout, vermilion prisms, m. p. 193° (Found : C, 57·0; H, 3·8. $C_{15}H_{12}O_6N_2$ requires C, 56·7; H, 3·9%).

We desire to thank the Carnegie Trust for the Universities of Scotland for a Scholarship which enabled one of us (J. M. G.) to take part in this investigation.

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CCI.—*The Rotatory Dispersive Power of Organic Compounds. Part XVII. β- and π-Sulphonic Derivatives of Camphor.*

By EVAN MATTHEW RICHARDS and THOMAS MARTIN LOWRY.

1. *Purpose of the Observations.*

THE experiments now described were undertaken in order to extend our knowledge of the rotatory dispersion of the derivatives of camphor, more particularly by including in the scope of our investigations a number of water-soluble compounds, since it appeared likely that the influence of the solvent would be reduced to a minimum when the optically active molecule is in a medium for which (just as in the case of a soap) it has no affinity except through the influence of a single ionisable group. Recent work on the orientation of the β-derivatives of camphor (this vol., p. 279)

has, however, made it possible also to draw important conclusions in reference to the influence of substitution on the dissymmetry of the camphor molecule in relation to its optical activity.

2. *Summary of Experimental Results.*

(a) *Abnormality of the π-Derivatives of Camphor.*—The data now recorded confirm the conclusion, already arrived at in the preceding paper (Part XVI) from the study of the halogen compounds, that there is something mysterious about the optical rotatory power of the π-derivatives of camphor. Thus, whereas the molecular rotatory powers of the α- and α′-bromo-derivatives of camphor and of β-bromocamphor differ by 425° and 540°, respectively (this vol., p. 1261), the corresponding derivatives of π-bromocamphor differ so little that the order of magnitude of their rotatory powers actually depends on the solvent chosen, the corresponding figure to those cited above being −47°. The present investigation has disclosed the further remarkable fact that, whilst the optical rotation of camphor, and of all the derivatives that have yet been examined (except camphorquinone), contains a high-frequency term (corresponding with the general absorption of a saturated molecule) and a low-frequency term (corresponding with the selective absorption of the unsaturated ketonic group), the rotatory power of many of the π-derivatives can be expressed, within the limits of experimental error, by a "simple" formula containing only a single low-frequency term. Thus the rotatory power of *ammonium α-bromocamphor-π-sulphonate*, $C_{10}H_{14}BrO{\cdot}SO_2{\cdot}ONH_4$ (Table I) in water agrees rigidly, over the whole range of the visual and photographic observations, with the theoretical values calculated from the "simple" dispersion equation $\alpha = 22{\cdot}015/(\lambda^2 - 0{\cdot}09668)$. The dispersion constant of this equation, $\lambda_0{}^2 = 0{\cdot}09668$ ($\lambda = 3109$ Å.U.), has the low frequency which is characteristic of the ketonic group, the high-frequency term of the parent ketone being reduced to such a small magnitude that it cannot be detected in the range of wave-lengths covered by the observations. The same behaviour was observed in *ammonium α-chlorocamphor-π-sulphonate*, $C_{10}H_{14}ClO{\cdot}SO_2{\cdot}ONH_4$ (Table II), the rotatory dispersion of which is also simple, and can be expressed completely, throughout the range covered by the visual and photographic observations, by the equation $\alpha = 17{\cdot}677/(\lambda^2 - 0{\cdot}09946)$, from which we can deduce the value $\lambda_0 = 3154$ Å.U. The photographic observations were less regular than in the case of the bromo-compound, but only because the settings of the analyser did not happen to correspond with strong lines in the iron spectrum.

In addition to these two salts, *α-bromocamphor-π-sulphonethyl-*

chloroamide,* $C_{10}H_{14}BrO\cdot SO_2\cdot NCl\cdot C_2H_5$ (Table III), and *α-bromocamphor-π-sulphondichloroamide*,* $C_{10}H_{14}BrO\cdot SO_2\cdot NCl_2$ (Table IV), gave a simple dispersion throughout the visible region (although in this case the curve was not followed into the photographic region), the value of the dispersion constant being $\lambda_0^2 = 0{\cdot}09969$ ($\lambda = 3157$ Å.U.) for the former and $\lambda_0^2 = 0{\cdot}10719$ ($\lambda_0 = 3200$) for the latter compound. An isomorphous mixture of the stereoisomeric *αα′-bromochlorocamphor-π-sulphonamides*,*

$$C_{10}H_{13}ClBrO\cdot SO_2\cdot NH_2,$$

the data for which are not reproduced, gave, however, a dispersion curve which, although it deviated only moderately from the simple law in the red, green, and blue regions, swung aside sharply in the violet, the dispersion being therefore obviously complex.

The predominance of the low-frequency term which is such a striking property of the π-sulphonic derivatives of camphor is not a completely new feature, since it can already be seen in the simple bromo-derivatives. Thus, whereas the two partial rotations of camphor are comparable in magnitude, the rotation constants of the low- and high-frequency terms being + 29·4 and — 20·1, respectively, the corresponding constants of απ-dibromocamphor are + 25·2 and — 5·7 only.

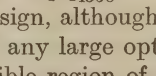
(b) *Properties of the β-Derivatives.*—Whereas the π-derivatives of camphor have an exceptionally high rotatory power, substitution in the β-position generally causes a diminution of rotatory power. Thus the rotatory power of Reychler's well-known camphorsulphonic acid, $C_{10}H_{14}O\cdot SO_2\cdot OH$ (Table V), in water, $[\alpha]_{5461} = +30{\cdot}4°$, $[M]_{5461} = +70{\cdot}7°$, is actually lower than that of camphor in benzene, $[\alpha]_{5461} = +52{\cdot}34°$, $[M]_{5461} = +79{\cdot}7°$ (compare β-bromocamphor, this vol., p. 1261). The dispersion of the acid is, however, obviously complex, since a simple formula which agrees with the data for the red and blue lines Zn 6362 and Zn 4811 shows a deviation of + 1·5° in the green, — 21° in the violet, and — 196° in the ultraviolet at 3969 Å.U. In this respect, the sulphonic acid closely resembles camphor itself; and it was found that by using the same dispersion constants as in the case of camphor (this vol., p. 612) a two-term formula could be fitted to the curve for the sulphonic acid with fairly good results, the maximum deviation in the photographic readings being about 2° in each case. Whereas, however, the deviations in the case of camphor were distributed irregularly as regards sign and magnitude, and were clearly within the limits of the errors of observation, the deviations in the case of the sulphonic acid (on readings of smaller magnitude) were obviously systematic, since the errors were all positive in the visual

* Available through the kindness of Prof. Pope and Mr. F. G. Mann.

region and all negative in the photographic region. A revised formula was therefore deduced in which the systematic errors were reduced to a small fraction of their former magnitude.* It should be noted that this was probably the only attempt that we have made to deduce the constants of a dispersion equation from external data, and that it was a failure, mainly because we were fortunate enough to be working with a long column of a strong aqueous solution of a transparent substance, so that our observed rotations were nearly twice as great as the specific rotations deduced from them.

As might be expected, the α-derivatives of Reychler's camphor-β-sulphonic acid show higher rotations than the parent compound. Thus potassium α-chlorocamphor-β-sulphonate, $C_{10}H_{14}ClO{\cdot}SO_2{\cdot}OK$ (Table VI), and potassium α-bromocamphor-β-sulphonate, $C_{10}H_{14}BrO{\cdot}SO_2{\cdot}OK$ (Table VII), gave *higher* rotations than camphor, namely, $[\alpha]_{5461} = +77{\cdot}4°$, $[M]_{5461} = +236°$ and $[\alpha]_{5461} = +111{\cdot}3°$, $[M]_{5461} = +389°$, respectively. The dispersions of these salts are complex but normal, the two partial rotations being of similar sign in each case.

The *sulphonamide*, $C_{10}H_{15}O{\cdot}SO_2{\cdot}NH_2$, of Reychler's acid is remarkable in being almost inactive, $[\alpha]_{5461} = +0{\cdot}4°$ only. It was therefore of interest to find out whether this small rotatory power was due to the small asymmetry of the compound, or to an anomalous dispersion, the small readings being then due merely to the observations falling in a region near to the wave-length at which an inversion of sign takes place. Observations for two other lines gave $[\alpha]_{5780} = -0{\cdot}8°$, $[\alpha]_{4358} = +15{\cdot}16°$, showing that there is actually a reversal of sign, although the rotations are still small, and do not indicate that any large optical rotatory power would be developed in the accessible region of the spectrum.

The *anhydramide*,  , of Reychler's acid (Table VIII) has a rotatory power, $[\alpha]_{5461} = -35{\cdot}9°$, $[M]_{5461} = -76{\cdot}5°$, of about the same magnitude as the parent compound, *but opposite in sign*, since the anhydramide derived from *d*-camphor is lævorotatory. The dispersion of this compound conforms closely to

* We are indebted to Mr. G. Owen, M.Sc., for this recalculation, which extended over a period of several months, and involved the investigation of more than a score of formulæ, before a satisfactory agreement was reached. The ultimate alteration in the constants was, however, relatively small, showing that a full series of readings fixes these constants within fairly narrow limits, thus:

	k_1.	k_2.	λ_1^2.	λ_2^2.
Old formula	21·523	−17·586	0·0872	0·0528
New formula	22·17	−18·32	0·085815	0·04945

Biot's law of inverse squares, but, on account of its small dispersion ratio, must be formulated as complex, just as in the analogous cases of sodium tartrate (Lowry and Austin, *Phil. Trans.*, 1922, *A*, **222**, 278) and octyl oxalate (Lowry and Richards, J., 1924, **125**, 1593). This observation is, however, of considerable interest in that, as a result of eliminating the ketonic double bond of camphor and replacing it by an imido-link in a closed ring, the *low-frequency term* in the dispersion equation has been reduced to a proportion which is almost negligible, whereas in the π-derivatives it is the *high-frequency term* which disappears from the equation.

3. *Relation between Rotatory Dispersion and Absorption.*

As in the case of Parts XV and XVI, publication of the dispersion data in the present paper has been delayed for more than a year in order to correlate them with measurements of absorption. A detailed comparison of the dispersion constants with the wave-lengths, λ_a, of the absorption bands now gives the results shown in the following table.

Dispersion Constants of Sulphonic Derivatives of Camphor.

	k_1.	k_2.	λ_1^2.	λ_2^2	λ_1.	λ_a.	$\lambda_1 - \lambda_a$.
Ammonium α-chlorocamphor-π-sulphonate	+17·677	—	0·09946	—	3150	3030	+120
Ammonium α-bromocamphor-π-sulphonate	+22·015	—	0·09668	—	3110	Am′ 3020 K′ 3040	+ 90
α-Bromocamphor-π-sulphonethylchloroamide	+25·889	—	0·09969	—	3160	—	—
α-Bromocamphor-π-sulphondichloroamide	+23·897	—	0·10719	—	3275	—	—
Camphor-β-sulphonic acid	+22·17	−18·32	0·08515	0·04945	2920	2850	+ 70
Camphor-β-sulphonanhydramide	—	−10·696	—	0*	—	—	—
Potassium α-chlorocamphor-β-sulphonate	+12·060	+ 5·1354	0·09768	—	3125	3000	+125
Potassium α-bromocamphor-β-sulphonate	+18·78	+ 5·569	0·09517	—	3085	3030	+ 55

* This compound conforms closely to Biot's law of rotatory dispersion.

In general, these constants follow one another fairly closely; thus Reychler's acid, which gives an abnormally small value for λ_1^2, is also seen to give an exceptionally small value for λ_a. As in all the cases hitherto examined, however, there is a steady discrepancy between the characteristic wave-lengths, λ_1 and λ_a,

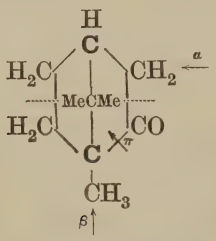
as deduced from the optical rotations and from the absorption spectra respectively. Since this discrepancy is in the same direction as in every previous case, and is, moreover, of the same order of magnitude, namely, 90 Å.U. as an average of five individual cases, it may now be regarded as a perfectly normal phenomenon. It therefore calls for no further comment, except to add that the " simple " one-term equations now worked out for some of the π-derivatives show just the same degree of concordance, and therefore rest on just as secure a foundation, as the " complex " two-term equations of the preceding paper of this series. In those cases, it was assumed in advance that the total rotation contains two partial rotations of unequal frequency; if a similar assumption were made in the present case, it would merely result in the development of equations in which $k_2 = 0$.

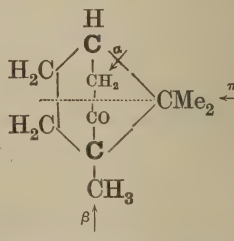
Attention may also be directed to the fact that camphor-β-sulphonanhydramide (in which the low-frequency partial rotation has disappeared from the equation as a sequel to eliminating the ketonic oxygen) is exceptionally transparent in the ultra-violet, and exhibits only a general absorption of light, without even a " step-out " to mark the presence of an incipient selective absorption (Lowry and Desch, J., 1909, **95**, 1343).

4. *Discussion of Experimental Results.*

In view of the proof that has recently been given (Wedekind, Schenk, and Stüsser, *Ber.*, 1923, **56**, 663; compare Lowry and Burgess, this vol., p. 279) that the β-derivatives, like the π-derivatives, are formed as a result of substitution in a methyl group, the three positions in which substitution can take place in the camphor molecule can be shown in two alternative aspects as in I and II :

(I.)





(II.)

Both methods of formulation bring out the fact that the molecule is almost symmetrical above and below the dotted horizontal line, and would indeed become completely symmetrical if (i) the >CO group were reduced to $>CH_2$, and (ii) the terminal methyl were replaced by hydrogen, or conversely. A still closer approach to symmetry can be seen in formula I, where the only element of

dissymmetry about a vertical plane perpendicular to that of the paper would again disappear if the CO group of camphor were reduced to CH_2.

(a) *Simple Dispersion of π-Derivatives.*—In summarising the experimental results it was stated that the rotatory dispersion of several of the π-derivatives can be expressed by means of a single term of Drude's equation, governed by a low-frequency dispersion constant only. In cases such as these, one may always suspect that the apparent simplicity of the low-frequency dispersion may mask the presence of a high-frequency term instead of eliminating it completely; but this does not excuse us from the necessity of inquiring why the high-frequency term has become impotent, or why this impotence should appear abruptly on passing from one group of compounds to another. The phenomenon to be accounted for is indeed very similar, whether the dispersion is fundamentally " simple " or only simple within the limits of experimental observation. In the analogous case of camphorquinone (J., 1924, **125**, 2511), the disappearance of the high-frequency term from the equation can be accounted for by noticing that (i) the low-frequency partial rotation of the unsaturated quinonoid group has a characteristic period in the visible spectrum, and therefore dominates completely the rotatory power of the molecule in the restricted region within which the compound is transparent, whilst (ii) the high-frequency partial rotation (which we attribute to the direct influence of the two asymmetric carbon atoms) is almost cancelled out by the growing symmetry of the molecule, since each asymmetric carbon atom is now adjacent to a CO group, and the only element of dissymmetry which remains is due to a contrast between hydrogen and methyl, so that *apo*camphorquinone (unlike *apo*camphor) would be optically inactive. In the case of the π-sulphonic derivatives these two asymmetric carbon atoms, which are already partly compensated in camphor itself, have been still more closely compensated by the introduction of symmetrically-placed sulphonic groups in the median plane between them, and therefore contribute only a negligible partial rotation to the total rotatory power of the molecule. In both cases, then, the disappearance of the high-frequency term can be associated with the approximate symmetry of the molecule about the median plane, just as in the case of camphoric anhydride, $C_8H_{14}\begin{matrix}<\mathrm{CO}\\ \mathrm{CO}>\end{matrix}O$, the specific rotatory power of which is less than 1° (Lowry, J., 1903, **83**, 968).

(b) *Induced Asymmetry in the π-Derivatives of Camphor.*—The increased magnitude of the low-frequency partial rotations, which is such a striking property of the π-derivatives, can be accounted

for by noticing the increased difference between the groups on either side of the vertical plane in formula II, since it is this difference alone which makes it possible to attribute an "induced asymmetry" to the ketonic group. A much more striking anomaly is, however, to be found in the fact that the reversal of sign of the >CHBr group in the α- and α′-derivatives, which has an enormous effect on the rotatory power of camphor, produces an almost negligible change in the rotatory power of the π-derivatives. A clue to the explanation of this curious fact may be found in the suggestion, put forward more than 20 years ago, in order to explain the reactivity of the methyl group in π-sulphonation, namely, the possible "formation of a direct linkage between the ketonic carbon and a median methyl" (Armstrong and Lowry, J., 1902, **81**, 1473). A

TABLE I.

Rotations of Ammonium α-Bromocamphor-π-sulphonate in Water at 20°.

13·936 G. in 100 c.c. of solution.
Length of tube 6 dcm.

$[\alpha] = 1{\cdot}1959 \times \alpha.$
$[M] = 3{\cdot}2816 \times [\alpha].$

$$[\alpha] = \frac{22{\cdot}015}{\lambda^2 - 0{\cdot}09668}.$$

	Visual readings.		[α] obs.	[α] calc.	[α] obs.—[α] calc.
Li	6708	+	62·49°	+ 62·32°	+0·2°
Cd	6438	+	69·09	+ 69·27	−0·2
Zn	6362	+	71·28	+ 71·46	−0·2
Na	5893	+	88·00	+ 87·91	+0·1
Cu	5782	+	92·51	+ 92·64	−0·1
Hg	5780	+	92·84	+ 92·73	+0·1
Cu	5700	+	96·45	+ 96·45	±
Hg	5461	+	109·40	+ 109·25	+0·2
Cu	5218	+	125·35	+ 125·37	±
Cu	5153	+	130·40	+ 130·37	±
Cu	5105	+	134·35	+ 134·26	+0·1
Cd	5086	+	135·93	+ 135·92	±
Zn	4811	+	163·37	+ 163·41	±
Cd	4800	+	164·67	+ 164·66	±
Zn	4722	+	174·43	+ 174·31	+0·1
Zn	4680	+	179·82	+ 179·93	−0·1
Cd	4678	+	180·29	+ 180·21	+0·1
Hg	4358	+	236·10	+ 236·06	±

Photographic readings.

Fe	*4306*	*+248·1*	*+248·2*	*−0·1*
	4258	*+260·0*	*+260·1*	*−0·1*
	4213	*+272·0*	*+272·4*	*−0·4*
	4172	*+283·9*	*+284·5*	*−0·6*
	4135	*+295·9*	*+296·4*	*−0·5*
	4068	*+319·8*	*+319·9*	*−0·1*
	4010	*+343·7*	*+343·4*	*+0·3*

TABLE II.

Rotations of Ammonium α-Chlorocamphor-π-sulphonate in Water at 20°.

20·440 G. in 100 c.c. of solution.
Length of tube 6 dcm.

$[\alpha] = 0{\cdot}81540 \times \alpha.$
$[M] = 2{\cdot}8370 \times [\alpha].$

$$[\alpha] = \frac{17{\cdot}677}{\lambda^2 - 0{\cdot}09946}.$$

		[α] obs.	[α] calc.	[α] obs.—[α] calc.
		+ 50·37°	+ 50·44°	−0·07°
		+ 56·03	+ 56·10	−0·07
		+ 57·89	+ 57·89	±
		+ 71·32	+ 71·38	−0·06
		+ 75·25	+ 75·26	−0·01
		+ 75·34	+ 75·34	±
		+ 78·39	+ 78·40	−0·01
		+ 88·97	+ 88·95	+0·02
		+102·32	+102·28	+0·04
		+106·53	+106·42	+0·11
		+109·60	+109·65	−0·05
		+111·10	+111·04	+0·06
		+133·96	+133·96	±
		+134·90	+135·01	−0·11
		+142·94	+143·10	−0·16
		+147·77	+147·83	−0·06
		+148·06	+148·06	±
		+194·70	+195·35	−0·65

Fe	*4315*	*+202·9*	*+203·8*	*−0·9*
	4277	*+211·0*	*+211·8*	*−0·8*
	4239	*+219·2*	*+220·3*	*−1·1*
	4204	*+227·3*	*+228·7*	*−1·4*
	4171	*+235·5*	*+237·3*	*−1·8*
	4150	*+243·6*	*+242·9*	*+0·7*
	4055	*+268·1*	*+265·9*	*+2·2*

TABLE III.

Rotations of α-Bromocamphor-π-sulphonethylchloroamide in Chloroform at 20°.

14·287 G. in 100 c.c. of solution.
Length of tube 2 dcm.
$[\alpha] = 3{\cdot}4997 \times \alpha.$
$[M] = 3{\cdot}7264 \times [\alpha].$
$$[\alpha] = \frac{25{\cdot}889}{\lambda^2 - 0{\cdot}09969}.$$

Visual readings.		[α] obs.	[α] calc.	[α] obs.−[α] calc.
Li	6708	+ 73·9°	+ 73·9°	±
Cd	6438	+ 82·3	+ 82·2	+0·1°
Zn	6362	+ 84·9	+ 84·9	±
Na	5893	+104·3	+104·6	−0·3
Cu	5782	+110·2	+110·3	−0·1
Hg	5780	+110·5	+110·5	±
Cu	5700	+114·4	+114·9	−0·5
Hg	5461	+130·4	+130·4	±
Cu	5218	+150·0	+150·0	±
Cu	5153	+156·0	+156·1	−0·1
Cu	5105	+160·6	+160·8	−0·2
Cd	5086	+162·8	+162·8	±
Zn	4811	+196·7	+196·5	+0·2
Cd	4800	+196·9	+198·0	−1·1
Zn	4722	+210·5	+210·0	+0·5
Zn	4680	—	—	—
Cd	4678	+217·3	+217·3	±
Hg	4358	+286·5	+286·8	−0·3

TABLE IV.

Rotations of α-Bromocamphor-π-sulphondichloroamide in Chloroform at 20°.

10·8716 G. in 100 c.c. of solution.
Length of tube 2 dcm.
$[\alpha] = 4{\cdot}5992 \times \alpha.$
$[M] = 3{\cdot}7905 \times [\alpha].$
$$[\alpha] = \frac{23{\cdot}897}{\lambda^2 - 0{\cdot}10719}.$$

		[α] obs.	[α] calc.	[α] obs.−[α] calc.
Li	6708	+ 69·7°	+ 69·7°	±
Cd	6438	+ 78·1	+ 77·8	+0·2°
Zn	6362	+ 80·9	+ 80·3	+0·6
Na	5893	+ 99·0	+ 99·6	−0·6
Cu	5782	+106·3	+105·2	+0·8
Hg	5780	+105·1	+105·3	−0·2
Cu	5700	+109·7	+109·8	−0·1
Hg	5461	+125·0	+125·1	−0·1
Cu	5218	+145·3	+144·7	+0·6
Cu	5153	+151·2	+150·9	+0·3
Cu	5105	+155·8	+155·7	+0·1
Cd	5086	+158·1	+157·8	+0·3
Zn	4811	+192·4	+192·4	±
Cd	4800	+194·5	+194·0	+0·5
Zn	4722	+205·7	+206·4	−0·7
Zn	4680	+213·4	+213·7	−0·3
Cd	4678	+215·0	+214·0	+1·0
Hg	4358	+286·0	+288·8	−2·8

TABLE V.

Rotations of Camphor-β-sulphonic Acid in Water at 20°.

28·636 G. in 100 c.c. of solution. Length of tube 6 dcm.
$[\alpha] = 0{\cdot}58202 \times \alpha.$ $[M] = 2{\cdot}3222 \times [\alpha].$
$$[\alpha] = \frac{22{\cdot}17}{\lambda^2 - 0{\cdot}08515} - \frac{18{\cdot}32}{\lambda^2 - 0{\cdot}04945}.$$

Visual readings.		[α] obs.	[α] calc.	[α] obs.−[α] calc.	Photographic readings.	[α] obs.	[α] calc.	[α] obs.−[α] calc.
Li	6707·85	+15·05°	15·03°	+0·02°	*Fe 4299*	*+ 87·06°*	*87·11°*	*−0·05°*
Cd	6438·47	+17·13	17·11	+0·02	*4246*	*+ 92·88*	*93·02*	*−0·14*
Zn	6362·35	+17·81	17·80	+0·01	*4192*	*+ 98·70*	*99·69*	*−0·99*
Na	5892·95	+23·11	23·11	±	*4155*	*+104·52*	*104·69*	*−0·17*
Cu	5782·16	+24·68	24·66	+0·02	*4114*	*+110·34*	*110·69*	*−0·35*
Hg	5780·13	+24·68	24·69	−0·01	*4078*	*+116·16*	*116·42*	*−0·26*
Cu	5700·25	+25·93	25·96	−0·03	*4041*	*+121·98*	*122·69*	*−0·71*
Hg	5460·74	+30·44	30·41	+0·03	*4014*	*+127·80*	*127·77*	*+0·03*
Cu	5218·70	+36·35	36·41	+0·06	*3982*	*+133·62*	*134·09*	*−0·47*
Cu	5153·25	+38·20	38·12	−0·08	*3969*	*+136·8*	*136·79*	*+0·01*
Cu	5105·54	+39·57	39·57	±				
Cd	5085·82	+40·25	40·21	+0·04				
Zn	4810·54	+51·07	50·90	+0·17				
Cd	4799·92	+51·61	51·39	+0·22				
Zn	4722·16	+55·46	55·33	+0·13				
Zn	4680·14	+57·65	57·60	+0·05				
Cd	4678·16	+57·84	57·68	+0·16				
Hg	4358·34	+81·24	81·15	+0·09				

Table VI.

Rotations of Potassium α-Chlorocamphor-β-sulphonate in Water at 20°.

12·386 G. in 100 c.c. of solution.
Length of tube 6 dcm.

$$[\alpha] = 1{\cdot}3456 \times \alpha.$$
$$[M] = 3{\cdot}0476 \times [\alpha].$$
$$[\alpha] = \frac{12{\cdot}060}{\lambda^2 - 0{\cdot}09768} + \frac{5{\cdot}1354}{\lambda^2}.$$

	Visual readings.	[α] obs.	[α] calc.	[α] obs.− [α] calc.
Li	6707·85	+ 45·75°	+ 45·65°	+0·10°
Cd	6438·47	+ 50·42	+ 50·45	−0·03
Zn	6362·35	+ 51·95	+ 51·95	±
Na	5892·95	+ 63·03	+ 63·16	−0·13
Cu	5782·16	+ 66·28	+ 66·32	−0·04
Hg	5780·13	+ 66·42	+ 66·38	+0·04
Cu	5700·25	+ 68·94	+ 68·88	+0·06
Hg	5460·74	+ 77·43	+ 77·37	+0·06
Cu	5218·70	+ 87·97	+ 87·93	+0·04
Cu	5153·25	+ 91·21	+ 91·18	+0·03
Cu	5105·54	+ 93·72	+ 93·71	+0·01
Cd	5085·82	+ 94·76	+ 94·77	−0·01
Zn	4810·54	+112·78	+112·37	+0·41
Cd	4799·92	+113·45	+113·15	+0·30
Zn	4722·16	+119·55	+119·35	+0·20
Zn	4680·14	+123·23	+122·72	+0·51
Cd	4678·16	+123·43	+122·99	+0·44
Hg	4358·34	+158·24	+157·74	+0·50
	Photographic readings.			
Fe	*4359*	*+158·24*	*+157·65*	*+0·59*
	4268	*+171·70*	*+170·95*	*+0·75*
	4185	*+185·15*	*+185·01*	*+0·14*
	4113	*+198·61*	*+199·05*	*−0·44*
	4055	*+212·07*	*+211·91*	*+0·16*
	3952	*+238·98*	*+239·02*	*−0·04**

* Deviation from simple formula $[\alpha] = 16{\cdot}699/(\lambda^2 - 0{\cdot}08335)$, obs. − calc. = + 10·0°.

Table VII.

Rotations of Potassium α-Bromocamphor-β-sulphonate in Water at 20°.

16·206 G. in 100 c.c. of solution.
Length of tube 6 dcm.

$$[\alpha] = 1{\cdot}0284 \times \alpha.$$
$$[M] = 3{\cdot}4922 \times [\alpha].$$
$$[\alpha] = \frac{18{\cdot}78}{\lambda^2 - 0{\cdot}09517} + \frac{5{\cdot}569}{\lambda^2}.$$

		[α] obs.	[α] calc.	[α] obs.− [α] calc.
		—	—	—
		+ 72·26°	+ 72·36°	−0·10°
		+ 74·43	+ 74·43	±
		+ 90·60	+ 90·61	−0·01
		+ 94·25	+ 94·20	+0·05
		+ 95·38	+ 95·30	+0·08
		+ 99·05	+ 98·90	+0·15
		+111·32	+111·20	+0·12
		+126·26	+126·50	−0·24
		+130·16	+131·16	−1·00
		+134·40	+134·85	−0·45
		+136·38	+136·10	+0·28
		+161·84	+161·93	−0·09
		+162·99	+163·07	−0·08
		+171·95	+171·92	+0·03
		—	—	—
		+177·24	+177·31	−0·07
		+227·35	+227·46	−0·11
Fe	*4306*	*+237·64*	*+238·14*	*−0·50*
	4260	*+247·92*	*+248·29*	*−0·37*
	4176	*+268·49*	*+269·25*	*−0·76*
	4101	*+289·06*	*+290·29*	*−0·23*
	4071	*+299·34*	*+299·75*	*−0·41*
	4041	*+309·63*	*+309·74*	*−0·11†*

† Deviation from simple formula $[\alpha] = 23{\cdot}891/(\lambda^2 - 0{\cdot}08379)$, obs. − calc. = + 9·1°.

Note.—The dispersion formulæ for these two compounds, which have been calculated by Mr. G. Owen, M.Sc., contain two partial rotations of similar sign, and therefore provide two more examples of the type of complex rotatory dispersion which has been described as "impossible to detect in practice" (compare footnote, this vol., p. 1262). The deviations from the simple formulæ (calculated to fit the red and blue zinc lines) are, however, already substantial even in the intermediate green region of the spectrum, and increase to about 2° in the case of the mercury violet line, and to about 10° at the extreme end of the visible spectrum; they are therefore far too obvious to be overlooked. This type of rotatory dispersion, although quite easy to detect in this series of compounds, is not common, since the induced asymmetry of the ketonic group is always opposite in sign to the fixed asymmetry of the camphor nucleus, except when the sign of the latter has been reversed by the creation of a new positive partial rotation as a result of introducing a substituent in the α-position.

Table VIII.

Rotations of Camphor-β-sulphonanhydramide in Acetone at 20°.

4·941 G. in 100 c.c. of solution. Length of tube 6 dcm.

$[\alpha] = 3{\cdot}3731 \times \alpha$. $[M] = 2{\cdot}1322 \times [\alpha]$. $[\alpha] = -10{\cdot}696/\lambda^2$.

Visual readings.		[α] obs.	[α] calc.	[α] obs.— [α] calc.	Visual readings.		[α] obs.	[α] calc.	[α] obs.— [α] calc.
Li	6708	−23·5°	−23·8°	+0·3°	Cu	5105	−41·0°	−41·0°	±
Cd	6438	−25·7	−25·8	+0·1	Cd	5086	−41·5	−41·4	−0·1°
Zn	6362	−26·4	−26·4	±	Zn	4811	−46·2	−46·2	±
Na	5893	−30·9	−30·8	−0·1	Zn	4722	−47·6	−48·0	+0·4
Cu	5782	−31·9	−32·0	+0·1	Cd	4678	−49·2	−48·9	−0·3
Hg	5780	−32·1	−32·0	−0·1	Hg	4358	−56·1	−56·3	+0·2
Cu	5700	−33·1	−32·9	−0·2	Photographic readings.				
Hg	5461	−35·9	−35·9	±	*Fe*	*4299*	*−57·8*	*−57·9*	*+0·1*
Cu	5218	−39·3	−39·3	±		*4220*	*−59·4*	*−60·1*	*+0·6*
Cu	5153	−40·6	−40·3	−0·3					

formula was then given which shows the formation of a new ring by the transference of a hydrogen atom from the π-methyl group to the ketonic oxygen; but it would be more in accord with our present views to postulate only a co-ordination of the reactive π-hydrogen atom with the ketonic oxygen. This co-ordination would have the advantage of enabling us to attribute the induced asymmetry of the ketonic group to a more concrete influence than that of a mere unsymmetrical field of force. It would, moreover, permit of a very simple explanation of the fact that the partial rotation of the ketonic group is always positive in sign, and is not even altered substantially in magnitude when the specific rotation of the molecule is shifted through several hundred degrees by reversing the sign of the >CHBr radical which is immediately adjacent to the ketonic group. In the π-derivatives this particular type of co-ordination is prevented by the elimination of the π-hydrogen atom; the two adjacent groups are therefore free to adjust themselves in such a way that a reversal of the fixed asymmetry of the saturated >CHBr group at once produces a compensating change in the induced asymmetry of the unsaturated >C=O group, whereby the balance of the molecule as expressed by its optical rotatory power is preserved almost unchanged.

5. *Summary.*

(*a*) The rotatory dispersion and absorption spectra of a series of β- and π-sulphonic derivatives of camphor have been determined. As in previous cases, there is a discrepancy of nearly 100 Å.U. between the characteristic frequencies deduced from the two series of observations.

(*b*) The rotatory dispersion of several of the π-derivatives can be expressed by one term of Drude's equation, the high-frequency

partial rotation being negligible in comparison with the magnitude of the low-frequency term, just as in the case of camphorquinone.

(*c*) The β-derivatives all exhibit complex dispersion, but the anhydramide nearly obeys Biot's law, since the low-frequency partial rotation and the band of selective absorption both disappear as a sequel to the elimination of the ketonic oxygen.

We are indebted to the Department of Scientific and Industrial Research for a maintenance grant to one of us (E. M. R.) during the period in which this research was carried out. We are also indebted to Prof. Pope and Mr. F. G. Mann for the loan of some of the compounds examined.

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CCII.—*Sulphur Sesquioxide.*

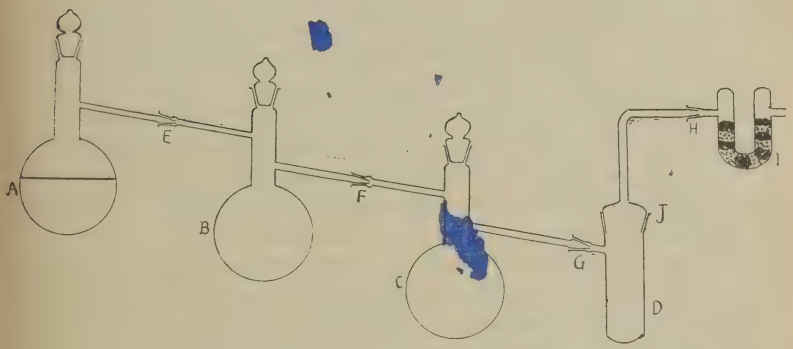
By ISRAEL VOGEL and JAMES RIDDICK PARTINGTON.

FROM the reaction between sulphur and sulphur trioxide Vogel (*J. Chem. Phys.*, 1812, **4**, 121) isolated a deep blue liquid, a bluish-green solid, and a brown liquid, all of which were considered to be definite compounds of sulphuric anhydride and sulphur. Similar results were obtained by Schweigger (*ibid.*, 1815, **13**, 484). Wach (*ibid.*, 1827, **50**, 1) endeavoured to determine the composition of the blue, green, and brown substances and found that the amount of sulphur combined with a definite quantity of sulphur trioxide increased in the order named. Fischer (*Ann. Phys. Chem.*, 1829, **16**, 119) and Rose (*ibid.*, 1834, **32**, 98) considered that the blue liquid contained a definite compound, whilst Berzelius ("Traité de Chimie," 1845, Tome I, p. 459) maintained that no new oxide of sulphur was present, and Stein (*J. pr. Chem.*, 1873, **6**, 172) ascribed the colour of the solution to the presence of finely divided sulphur. Weber (*Ann. Phys. Chem.*, 1875, **156**, 531) found the sulphur content of the bluish-green solid to correspond with S_2O_3. No further work appears to have been done, and the current view seems to be that the supposed sulphur sesquioxide is a "colloidal solution" (compare Hofmann, "Anorganische Chemie," 1920, p. 166; Ephraim, "Anorganische Chemie," 1922, p. 437). The present research was accordingly undertaken with the object of definitely deciding between these two theories and of studying the properties of the substance if it were proved to be a chemical compound.

The starting materials of previous investigators were far from pure, and this was probably the cause of the different results obtained.

Purification of Sulphur.—The purest commercial precipitated sulphur was distilled in a Pyrex retort in a current of pure carbon dioxide, the distillate being collected and allowed to solidify in a Jena glass flask; the first and last fractions were neglected. The distillate was melted and the liquid poured on to watch-glasses of Jena glass, the melting and cooling being conducted in an atmosphere of dry carbon dioxide. When the sulphur had almost completely resolidified, it was cut up into small pieces and the above process repeated three times, considerable head and tail fractions being discarded in each distillation. After the first distillation, the sulphur did not darken appreciably but melted to a clear and mobile liquid which, with rise of temperature, exhibited all the usual phenomena, but did not darken appreciably. The purified sulphur

FIG. 1.



was finely powdered and preserved in a vacuum desiccator over phosphorus pentoxide until required.

Preparation of Pure Sulphur Trioxide.—Although many types of apparatus have been devised and employed for the preparation of pure sulphur trioxide (compare Weber, *Ann. Phys. Chem.*, 1876, **159**, 313; Divers and Shimosé, *Ber.*, 1883, **16**, 1009; Schenk, *Annalen*, 1901, **316**, 1; Lichty, *J. Amer. Chem. Soc.*, 1908, **30**, 1834; Beckmann, *Z. anorg. Chem.*, 1912, **77**, 90), none of these permit of the preparation of large quantities of the anhydride in a comparatively short time, nor do they allow of the convenient handling of the pure product. The apparatus shown in Fig. 1 was constructed for the preparation of pure sulphuric anhydride from oleum. The apparatus was entirely of Durosil resistance glass. The three distilling flasks, A, B and C, and a reaction vessel D were connected by interchangeable ground joints. Stoppers were ground to fit the mouths of the flasks and reaction vessel and also both parts of the joints E, F and G so that any flask or flasks could be

removed from the remainder of the apparatus without access of moisture. A phosphorus pentoxide drying tube, I, was attached to the reaction vessel by means of the joint H.

Kahlbaum's pure 65% oleum (about 200 c.c.) was placed in A, B was immersed in a bath of ice-cold water, C surrounded by a freezing mixture of finely-ground ice, and the bath of concentrated sulphuric acid surrounding A was very carefully warmed. Sulphur trioxide distilled over and condensed in B, only a very small quantity finding its way to C. The sulphuric anhydride which passed over on gentle heating was the only portion collected. After distillation and some cooling, the flask A was detached at E and immediately replaced by a ground glass stopper. B was then placed in the sulphuric acid bath, C surrounded by cold water, D immersed in a freezing mixture of ice and salt, and the bath surrounding B very gently warmed. Sulphur trioxide distilled into C, the distillation being stopped when about three-quarters of the contents of B had passed over : flask B was then removed and replaced by a ground glass stopper. Flasks B and A after cleaning and drying were then attached to the apparatus and the distillation was repeated in the manner described. In this way, pure sulphur trioxide was obtained, two to three distillations usually being sufficient. It melted completely at about 15° to a colourless liquid and crystallised on cooling in beautiful needles.

To transfer the anhydride to the reaction vessel, the solid was melted and the flasks were rotated about the ground glass joints.

Preparation and Analysis of Sulphur Sesquioxide.—A mode of procedure similar to that described by Weber (*Ann. Chem. Phys.*, 1875, **156**, 531) was first employed. About 20 c.c. of liquid sulphuric anhydride were placed in the reaction vessel and the latter was closed by a ground glass stopper at G. Sulphur was then added in small quantities by momentarily detaching the ground glass joint J, a fresh portion being added only after the previous quantity had entered into combination. The sulphur on coming in contact with the anhydride formed blue drops, most of which sank, but some became attached to the sides of the vessel near the surface of the sulphur trioxide. In order to avoid formation of a cake of solid at the surface, the vessel must be shaken during the preparation, when most of the substance sinks as soon as formed. If the sulphur be added too rapidly, the temperature of the sulphuric anhydride rises and the solid near the surface decomposes with the evolution of sulphur dioxide. If, however, the vessel be shaken during the addition and care be taken that the temperature does not rise above 15°, very little decomposition occurs. After about 1 or 2 g. of sulphur had been added, the excess of liquid sulphur trioxide,

which should be colourless, was poured off and any still remaining removed by warming in a vacuum at 30—40°, two towers, containing concentrated sulphuric acid on pumice and borax on glass wool respectively, being interposed before the pump. All the sulphuric anhydride could not be easily removed in this manner and it was necessary first to powder the bluish-green substance in an atmosphere of dry carbon dioxide and then to heat in a vacuum as described. Weber's compound probably contained small quantities of occluded sulphur trioxide, since he attempted to remove the latter merely by warming to " blood " temperature.

The substance thus obtained was a bluish-green solid, which soon decomposed at the ordinary temperature with the evolution of sulphur dioxide, sulphur remaining. Decomposition was accelerated by warming. The compound was very hygroscopic; if left exposed to the air, decomposition occurred and moist sulphur remained. If all the sulphuric anhydride had been removed, the substance was stable for several minutes at about 15°. In carrying out the analyses the weighings were performed as rapidly as possible.

Weber's method of analysis (*loc. cit.*) was first repeated and confirmed. Some of the substance was weighed out into a small glass-stoppered tube and, after removing the stopper, the tube was allowed to slide down the side of another but larger glass-stoppered vessel containing a mixture of concentrated and fuming nitric acids, great care being taken that the acid did not reach the contents of the small tube. The larger tube was then stoppered and completely wrapped in a cloth, since explosions sometimes resulted. The vessel was inclined so that the acid came in contact with the substance; a violent reaction ensued, and the stopper was held down. The whole was allowed to stand over-night. The contents of the tube were then diluted and the precipitated sulphur was collected on a weighed Gooch crucible. The sulphur in the filtrate was estimated, after the nitric acid had been boiled off, with barium chloride solution in the usual manner. The results are given in Table I.

TABLE I.

G. of substance.	G. of precipitated S.	G. of $BaSO_4$-S.	Total percentage of S.
0·4272	0·1074	0·1365	57·09
0·5870	0·1484	0·1876	57·24
0·5106	0·1202	0·1722	57·27
		Calculated for S_2O_3	57·19

In another method of analysis the sulphur of the compound was oxidised to sulphuric acid in one operation by a mixture of fuming nitric acid and bromine, the operation being carried out in the manner described. Of some twenty-five analyses carried out by this method, four exploded. A few typical results are

recorded in Table II : all the successful analyses were between the limits of 56·96 and 57·81% sulphur.

TABLE II.

G. of substance.	G. of $BaSO_4$.	G. of S.	Total percentage of S.
0·2103	0·8775	0·1206	57·32
0·5105	2·1671	0·2977	57·31
0·3030	1·2605	0·1732	57·15
0·4900	2·0356	0·2797	57·08
0·1696	0·7055	0·0969	57·15
		Calculated for S_2O_3	57·19

The results are in agreement with those found by the first method and with the value required by S_2O_3. It appears, therefore, that the substance has a constant chemical composition.

The method of preparation of the compound given above is somewhat laborious and cannot be used for the preparation of comparatively large quantities. It was found that instead of adding the sulphur to the liquid sulphuric anhydride, one might add the latter to the former and obtain a similar result. About 1 g. of finely-powdered sulphur was placed in the reaction vessel and about 15 c.c. of liquid sulphur trioxide were added. No reaction appeared to take place at first, although the whole assumed a deep blue colour and became somewhat viscid. After approximately 30 seconds, a violent reaction set in, so that it was found advisable to detach the phosphorus pentoxide tube from the reaction vessel, clouds of white fumes being evolved. After about 2 minutes the reaction subsided, the supernatant liquid sulphuric anhydride, which was coloured very pale blue, was poured off, and the residual sulphur trioxide removed from the resultant bluish-green solid in the manner already described. The bluish-green solid * thus obtained dissolved in oleum with the production of a deep blue solution, decomposed on exposure to air and on keeping with the evolution of sulphur dioxide, absorbed moisture from the air, and appeared to be identical with the substance prepared by the first method. The analysis by the fuming nitric acid and bromine method yielded the following results :

TABLE III.

G. of substance.	G. of $BaSO_4$.	G. of S.	Total percentage of S.
0·1994	0·8296	0·1140	57·16
0·2316	0·9660	0·1327	57·30
0·1778	0·7406	0·1017	57·22
		Calculated for S_2O_3	57·19

This method of preparation is simpler and more convenient than the first one, and the residual sulphuric anhydride from one preparation

* On some occasions the solid was green.

may be employed again for the conversion of another quantity of sulphur into the sesquioxide.

Owing to the great instability of the compound a number of experiments were performed with a view to render it more stable. It was found that the solid could be kept unchanged for several hours in a completely dry oxygen-free atmosphere at low pressures (less than 1 mm. of mercury). Cooling to liquid air temperatures had no appreciable effect.

The empirical formula of the compound has been shown to be $(S_2O_3)_x$, which for the sake of simplicity was taken as S_2O_3. From this it would seem that the substance might be the anhydride of hyposulphurous acid, but it may be said at once that all attempts to convert it into either the acid or its simple derivatives failed, owing to the simultaneous side and consecutive reactions and the production of mixtures of complicated sulphuroxy-acids, the reactions and identification of which are described below.

It was thought that the formula of the compound might be established by processes similar to those employed by Bernsthen (*Annalen*, 1881, **208**, 142) for sodium hyposulphite, but it was found that substances are formed in solution which complicate the reactions and that no evidence as to the constitution of the substance can be obtained from these results.

The molecular weight of the substance was not determined, since no solvent could be found with which the compound did not react. Purified phosphorus oxychloride, the only pure solvent for sulphuric anhydride at present known (compare Lichty, *J. Amer. Chem. Soc.*, 1912, **34**, 1441), caused complete decomposition of the sulphur sesquioxide.

Owing to the extremely reactive and unstable nature of the substance, all attempts to deduce its constitution by methods usually applicable to acid anhydrides were unsuccessful. Nevertheless, the results obtained could be completely reconciled with the formula S_2O_3 for the original compound.

Properties of Sulphur Sesquioxide.—Sulphur sesquioxide dissolves in oleum with the formation of a deep blue solution identical with that produced by the addition of sulphur. A solution of indigo in concentrated sulphuric acid or of indigo-carmine in water is partially decolorised; in no case could complete decoloration be effected even by the addition of comparatively large quantities of the substance. A similar reaction takes place with strongly ammoniacal copper sulphate solution, the decoloration being only partial.

With anhydrous ether a violent reaction takes place, the compound decomposing with the separation of sulphur and the production of a yellow solution; on decanting the clear, evil-smelling

liquid and distilling off the ether, a very small quantity of a yellow oil remained. The amount, however, was too small for analysis and qualitative tests pointed to the presence of sulphur.

A similar reaction takes place with absolute (100%) ethyl alcohol. Here a very small quantity of a pale yellow liquid was obtained after removal of the separated sulphur by filtration and the alcohol by distillation. The amount was too small for analysis, but qualitative tests indicated the presence of sulphur.

Sulphur sesquioxide when allowed to come into contact with water decomposes, a pale yellow solution (compare hyposulphurous acid) being momentarily formed, the decomposition being accompanied by a loud hissing noise and the simultaneous formation of a milky solution due to the separation of sulphur. If a relatively large quantity of the sesquioxide be employed, yellow sulphur separates, which when freshly formed is somewhat plastic, but soon becomes brittle. The filtered solution contained sulphuric acid and trithionic acid, together with small quantities of penta- and possibly tetra-thionic acids, as detected by the reactions with mercurous nitrate, cupric sulphate, mercuric chloride, and ammoniacal silver nitrate solutions, respectively (compare Takamatsu and Smith, J., 1880, **37**, 592; Debus, J., 1888, **53**, 278; Riesenfeld and Feld, *Z. anorg. Chem.*, 1921, **119**, 225; Forster and Hornig, *ibid.*, 1922, **125**, 86), whilst the presence of sulphurous acid was indicated by the coloration with ferric chloride solution. The yellow coloration with ferric chloride solution is not, however, exclusive to sulphurous acid (compare Debus, *loc. cit.*), but is also produced by sulphoxylic acid and its salts (*vide infra*), hence both these substances may have been present. That the yellow coloration is due to a substance other than sulphurous acid is probable, since after removing the latter by the passage of a current of air through the solution for several hours, the residual liquid gave a yellow coloration with ferric chloride. The complete removal of sulphur dioxide was detected by inserting two flasks, the first containing a known volume of standard iodine solution and the second a known volume of standard thiosulphate solution, before the pump, and titrating : the total quantity of iodine remained unaltered when the process was complete. The quantities of tetra- and pentathionic acids increased with time, as was shown by the yellow opalescence produced on the addition of the first few drops of mercurous nitrate solution. No qualitative tests are at present known by which small quantities of tetrathionic acid or its salts may be detected in the presence of pentathionic acid or its salts, hence the conclusion as to the presence of tetrathionic acid in the solution is somewhat doubtful.

The initial reaction with water may consist in the decomposition of the sulphur sesquioxide into monoxide and dioxide :

$$S_2O_3 = SO + SO_2.$$

Some of the monoxide polymerises, the polymeride in the presence of water forming pentathionic acid :

$$5SO + H_2O = H_2S_5O_6$$

(compare Debus, *loc. cit.*; Riesenfeld and Feld, *loc. cit.*), whilst another portion reacts with water to produce sulphoxylic acid :

$$SO + H_2O = H_2SO_2.$$

The chief reaction, however, consists in the formation of trithionic acid; two modes of interaction are possible, the first being between water, sulphur sesquioxide and sulphur dioxide :

$$S_2O_3 + SO_2 + H_2O = H_2S_3O_6,$$

and the second between sulphur monoxide, sulphur dioxide and water :

$$SO + 2SO_2 + H_2O = H_2S_3O_6.$$

The latter reaction probably take place to the greater extent. If the solution be kept for some time, the trithionic acid gradually combines with *nascent* sulphur with the production of tetra- and penta-thionic acids :

$$H_2S_3O_6 + S = H_2S_4O_6;$$
$$H_2S_4O_6 + S = H_2S_5O_6;$$
$$H_2S_3O_6 + 2S = H_2S_5O_6.$$

The last reaction to be studied was that with an anhydrous alcoholic solution of sodium ethoxide, prepared by adding sodium to absolute ethyl alcohol in a Jena flask fitted with a reflux condenser and phosphorus pentoxide drying tube. On addition of sulphur sesquioxide, an extremely vigorous reaction took place, small quantities of a yellow, crystalline solid separating out and the whole liquid assuming a yellowish-brown colour. The product of the reaction had a very strong and unpleasant odour somewhat resembling that of garlic and affecting the voice if the vapour was inhaled for any length of time. On adding sulphuric acid immediately after the reaction a white solid was precipitated, which was separated by adding absolute alcohol, filtering, and drying over phosphorus pentoxide. The solid was fairly soluble in water, neither the solution nor the solid decolorising indigo or ammoniacal cupric sulphate solutions. Qualitative tests indicated the presence of sulphur and sodium. The sodium was determined as sulphate,

whilst the sulphur was estimated by fusion with a mixture of sodium peroxide and sodium carbonate (Treadwell-Hall, "Quantitative Analysis," 1919, p. 849) and in a second process by oxidation with a mixture of fuming nitric acid and bromine, as detailed above. The latter method is much more convenient than the first. The results of the analyses agreed fairly well with those required by *sodium ethyl sulphoxylate* (Found : Na, 20·10, 20·06; S, 27·80, 27·85. $NaEtSO_2$ requires Na, 19·81; S, 27·61%).

Unless extreme precautions are taken to prevent the access of moisture, and unless the substance is isolated immediately after the reaction, the resulting solid consists of a mixture of sodium ethyl sulphoxylate and its hydrolysis product. The completely hydrolysed product was isolated from the solution by allowing it to stand over-night and then gradually acidifying with dilute sulphuric acid; a yellow precipitate separated which became white as soon as the whole solution was acid. The precipitate was immediately filtered with the aid of the pump, washed with absolute alcohol, and dried over phosphorus pentoxide for a week. A perfectly white, crystalline solid was obtained which remained unchanged when heated at 110° for 2 hours. The sulphur content was determined by the fuming nitric acid and bromine method; in the estimation of sodium the substance was first decomposed with a boiling mixture of fuming nitric acid and bromine, evaporated to small bulk, diluted with water, and transferred to a weighed platinum dish, the estimation for sodium as sulphate being continued in the usual manner (Found : Na,40·24, 41·08, 41·04; S, 29·16, 29·20, 29·14. Na_2SO_2 requires Na, 41·80; S, 29·13%).

Sodium sulphoxylate is moderately soluble in cold and more soluble in hot water and sparingly soluble in alcohol. It is practically unattacked by boiling concentrated hydrochloric and sulphuric acids, but is attacked by a hot mixture of fuming nitric acid and bromine. The aqueous solution gives a yellow coloration with ferric chloride solution. On exposure to air, the white solid assumes a yellowish-brown colour.

The filtrate from the preparation of sodium sulphoxylate, which still possessed a strong unpleasant odour, was found to contain salts of trithionic, sulphoxylic, and sulphuric acids, and also small quantities of penta- and possibly tetra-thionic acids. The product of the reaction between sulphur sesquioxide and sodium ethoxide has a strongly alkaline reaction and under these conditions it would be expected that any tetra- and penta-thionates formed would decompose with the formation of sulphites and thiosulphates, but the absence of the latter clearly proved that very little, if any, of these substances had been produced in the initial reaction.

The reactions which take place may be represented as follows :

(1) $S_2O_3 = SO + SO_2$.
(2) $SO + NaOEt = NaEtSO_2$.
(3) $NaEtSO_2 + NaOH = Na_2SO_2 + EtOH$.

Some of the sulphur monoxide or sesquioxide may react thus :

(4) $SO + 2SO_2 + NaOEt = NaEtS_3O_6$ or
(4a) $S_2O_3 + SO_2 + NaOEt = NaEtS_3O_6$.
(5) $NaEtS_3O_6 + NaOH = Na_2S_5O_6 + EtOH$.

The very small quantity of pentathionate present may be formed by the polymerisation of the sulphur monoxide :

(6) $5SO + NaOEt = NaEtS_5O_6$.
(7) $NaEtS_5O_6 + NaOH = Na_2S_5O_6 + EtOH$

or more probably by the decomposition of the trithionate :

(6a) $5Na_2S_3O_6 = Na_2S_5O_6 + Na_2S_4O_6 + 3Na_2SO_4 + 3SO_2$

(compare Debus, *loc. cit.*). The unpleasant odour of the solution may be due to the sodium ethyl salts present.

Attempt to isolate Sulphur Monoxide, SO.—Divers and Shimosé (*Ber.*, 1883, **16**, 1009) showed that the analogous tellurium compound, tellurium sulphoxide, $STeO_3$, decomposes when gradually heated in a vacuum to 235° with the production of tellurium monoxide; $STeO_3 = TeO + SO_2$, as confirmed by J. J. Doolan and one of us (J., 1924, **125**, 1403). It was possible that a similar reaction might take place with sulphur sesquioxide, although it was expected that the resulting sulphur monoxide would, if formed, be very much less stable. Sulphur sesquioxide was placed in a small Jena flask, and the latter exhausted to a pressure below 1 mm. of mercury. The flask was then gradually heated in a metal bath. As the temperature rose, the bluish-green solid slowly changed colour and signs of appreciable decomposition were apparent at about 70° : decomposition was complete at 95°. On further heating, the residue melted to an amber-coloured liquid which exhibited all the properties of sulphur.

It is possible that by employing a slower rate of heating in a very high vacuum from which all traces of moisture and oxygen have been excluded, sulphur monoxide might be isolated.

The "Colloidal Solution" Theory.—Although in the light of the experiments described in this paper there is little doubt that the bluish-green solid obtained by the interaction of sulphur and liquid sulphur trioxide is a definite chemical compound and not a "colloidal solution," it was considered advisable to obtain further evidence

against the latter view. Stress must be laid on the fact that pure sulphur is *insoluble* in pure sulphuric anhydride, although combination occurs with the formation of sulphur sesquioxide, which is also practically insoluble. It is only in the presence of small quantities of water that the substance dissolves to a blue solution.

Liquid sulphuric anhydride was added to sulphur contained in a glass tube, no precautions being taken to exclude moisture. After the violent reaction was over, the blue solution was poured off. An intense beam of light from a lantern was passed through the solution, but no Tyndall cone was visible.

If concentrated sulphuric acid be added gradually to the blue solution, and the latter examined after each addition for a Tyndall cone, it will be found that at a certain point corresponding to the green and brown solutions a marked Tyndall cone is visible, indicating that a substance (sulphur) of ultramicroscopic dimensions has separated. Further addition of sulphuric acid results in the separation of sulphur in a form visible to the naked eye.

Some of the blue liquid was carefully poured into water, and the resultant solution filtered from the precipitated sulphur. The filtrate contained trithionic acid (the main constituent), penta- and possibly tetra-thionic acids, sulphurous, sulphoxylic and sulphuric acids. If the deep blue solution be poured into a concentrated solution of potassium acetate, large quantities of potassium trithionate and little, if any, potassium tetra- and penta-thionates are present in the solution. It appears, therefore, that the tetra- and penta-thionates are produced from trithionates and nascent sulphur. Similar results are obtained with the green and brown solutions. One can accordingly conclude that the blue liquid is a *molecular* solution of sulphur sesquioxide in oleum, whilst the other coloured liquids produced by the dissolution of sulphur in fuming sulphuric acid of certain strengths are mixtures of colloidal solutions of sulphur and molecular solutions of sulphur sesquioxide.

In conclusion, the authors express their indebtedness to the Chemical Society for a grant which has partly defrayed the expenses incurred in the research.

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CCIII.—*The Parachor and Chemical Constitution. Part I. Polar and Non-polar Valencies in Unsaturated Compounds.*

By Samuel Sugden, John Brent Reed, and Henry Wilkins.

(1) *Double Bonds and the Parachor.*

A new method of comparing molecular volumes by the use of a constant termed the "parachor" has been suggested by one of us (Sugden, J., 1924, **125**, 1177), who showed that this quantity is an additive function of certain atomic and structural constants by means of which the experimental values for a large number of organic compounds can be predicted with considerable accuracy.

Amongst the structural constants there evaluated is the effect of a double bond, which was found to add 23·2 units to the molecular parachor. Some of the data for this type of linking are given in Table I. The values of $[P]$ obs. given in the fourth column are calculated from observations by the investigators indicated by initials in the third column; full references are tabulated on p. 1535. The fifth column, headed $\Sigma[P]$, gives the sum of the atomic constants, and by subtracting this from the observed parachor the constant for the double bond in the last column is obtained.

Table I.

Parachor of non-polar double bonds.

Substance.	Formula.	Observer.	$[P]$ obs.	$\Sigma[P]$.	Double bond.
Ethylene	C_2H_4	M. & W.	99·5	78·0	21·5
Propylene	C_3H_6	,,	139·9	117·0	22·9
Amylene	C_5H_{10}	Sch.	218·2	195·0	23·2
Diallyl	C_6H_{10}	,,	248·2	199·8	$2 \times 24·2$
Acetone	C_3H_6O	M. & O.	160·9	137·0	23·9
Methyl ethyl ketone	C_4H_8O	,,	198·2	176·0	22·2
Diethyl ketone	$C_5H_{10}O$	,,	236·2	215·0	21·2
Methyl propyl ketone	,,	M. & S.	238·0	,,	23·0
Dipropyl ketone	$C_7H_{14}O$	M. & K.	314·1	293·0	21·1
Methyl hexyl ketone	$C_8H_{16}O$	M. & O.	355·7	332·0	23·7

This type of double linking has been found in a large number of organic compounds and gives an average increase of 23·2 units in the molecular parachor. The same value is found for double bonds between carbon and carbon, carbon and oxygen, carbon and sulphur, and nitrogen and oxygen atoms.

We have recently investigated a number of compounds of nitrogen, phosphorus, and sulphur, and have found several anomalous cases in which the presence of a double bond appears to have little or no effect on the parachor. The nitrogen compounds will be discussed

later; data for nine compounds of phosphorus and sulphur which show this anomaly are collected in Table II.

The atomic parachors for phosphorus and sulphur used in this table are $P = 37{\cdot}7$, and $S = 48{\cdot}2$; data on which they are based are presented on p. 1533. These values are consistent with those found for neighbouring elements in the periodic table

C.	N.	O.	F.	Si.	P.	S.	Cl.
4·8	12·5	20·0	25·7	12·0	37·7	48·2	54·3

and indicate a periodic variation of atomic parachors with increasing atomic number similar to the well-known property of atomic volume.*

The data presented in Tables I and II provide definite experimental evidence of the existence of two kinds of double bond, one, common in carbon compounds, but found also in compounds of other elements, which causes an increase in the parachor of 23·2 units, and another, present in derivatives of the oxyacids of sulphur and phosphorus, which lowers the molecular parachor by 1·6 units.

TABLE II.

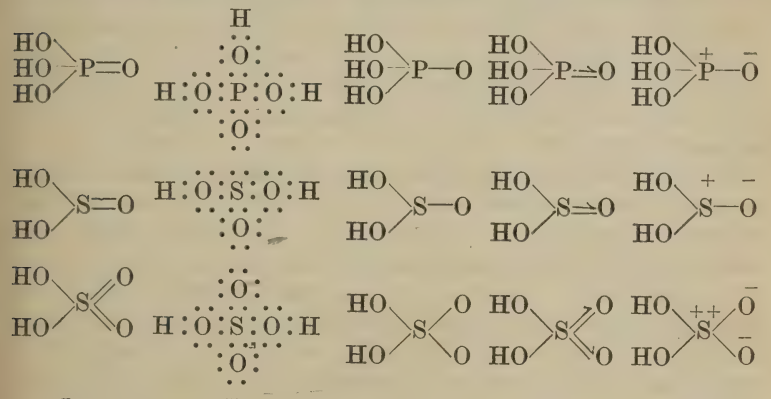
Parachor of semipolar double bonds.

Substance.	Formula.	Observer.	[P] obs.	Σ[P].	Double bond.
Phosphorus oxychloride	$Cl_3P \rightleftharpoons O$	S. R. & W.	217·6	220·6	− 3·0
		R. & S.	217·6	,,	− 3·0
Triethyl phosphate	$(EtO)_3P \rightleftharpoons O$	S. R. & W.	399·1	403·0	− 3·9
Triphenyl phosphate ...	$(PhO)_3P \rightleftharpoons O$	,,	686·5	687·7	− 1·2
Thionyl chloride	$Cl_2S \rightleftharpoons O$	,,	174·5	176·8	− 2·3
		R. & S.	(172·5)	,,	(− 4·3)
Sulphuryl chloride		S. R. & W.	193·3	196·8	− 1·65 × 2
		R. & S.	(187·0)	,,	(4·9 × 2)
Diethyl sulphite		W. & S.	299·7	298·4	+ 1·3
Ethyl ethanesulphonate		,,	295·8	,,	− 1·3 × 2
Dimethyl sulphate		S. R. & W.	238·9	240·4	− 0·75 × 2
Diethyl sulphate		,,	313·8	318·4	− 2·3 × 2
				Mean	− 1·6

* The variation of the parachor with atomic number will be discussed more fully in a subsequent paper.

(2) *Electron Valency Theories.*

The compounds discussed in Table II belong without exception to the class in which the octet valency theories of Lewis (*J. Amer. Chem. Soc.*, 1916, **38**, 762) and Langmuir (*ibid.*, 1919, **41**, 868, 1543; 1920, **42**, 274) lead to a modification of the usual structural formulæ. The electronic formulæ for phosphoric, sulphurous, and sulphuric acids are indicated in formulæ II; if a valency bond is written for each pair of shared electrons, then formulæ III are obtained which



(I.) (II.) (III.) (IV.) (V.)

do not exhibit the double bonds found in the usual formulæ I. It has been pointed out by Lowry (*Trans. Faraday Soc.*, 1923, **18**, 285) that in formulæ II the oxygen atom sharing two valency electrons and holding six others will be negatively charged and that, therefore, a double bond is present but consists of one covalency and one electrovalency. Lowry suggests two methods (IV and V) of formulating this type of linking; we have in most cases used the first of these methods in which a barb on the valency bond indicates the direction in which an electron has been transferred. This choice was largely determined by the consideration that formulæ of type V are apt to be confused with other formulæ in current use in which + and − signs are attached to atoms without removing a valency bond and so do not indicate an electrovalency.

Lowry has proposed the terms "mixed" or "ionised" double bonds for the linking present in formulæ IV and V. The second of these has been criticised by Porter, and by Rankine (*Trans. Faraday Soc.*, 1923, **18**, 296) on the grounds that no free ions are present, and the term "mixed" is somewhat indefinite. The nomenclature of Lewis (*loc. cit.*) for the two kinds of single bond, namely, polar valencies and covalencies, is now in common use, and in conformity with this we propose to term the double bond

consisting of one covalency and one electrovalency a semipolar double bond. The linking commonly found in carbon compounds which consists of two covalencies will be termed a non-polar double bond.

That two kinds of double bond do exist is shown clearly by the experimental evidence summarised in Tables I and II. Further, from the fact that all the substances in Table II must, on the octet theory, contain semipolar double bonds it is evident that a parachor of — 1·6 must be assigned to this linking. The double bond with a parachor of 23·2 which is common in carbon compounds must therefore be identified as the non-polar double bond. The effect of these two types of linking on the parachor is readily understood when it is remembered that this constant is a measure of the molecular volume.

When any additive relation is analysed and reduced to a series of atomic and structural constants it is well known that the effect of a single bond cannot be separately evaluated and the assumption is usually made that the constant for this linking is zero. In the first paper on the parachor, this practice was followed and the atomic parachors there obtained include the effect, if any, of a single bond. The semipolar double bond consists of a covalency with a superimposed electrovalency; its effect should therefore be that of a single bond, which is taken as zero, plus the effect of the electrostatic attraction between the two charged atoms, which should cause a contraction in volume. This contraction would not be large, since it appears improbable that considerable distortion of the outer shells of electrons could occur. It is significant that with one exception all the substances in Table II give a negative value for the parachor of a semipolar double bond. The mean value, — 1·6, is of the same order of magnitude as the deviations of individual values from this mean, but the balance of evidence seems to be in favour of a real but small negative value for the contribution of this linking to the parachor.

For the non-polar double bond there is the large expansion in volume of 23·2 units. The original cubical atom of Lewis (*loc. cit.*) would give a smaller volume for two cubes placed face to face than for two cubes edge to edge. The statical theory of atomic structure is, however, quite incapable of accounting for all the modern work on spectra and atomic structure and in particular the successful application of relativity considerations to the explanation of the fine structure of spectral lines seems to provide conclusive evidence in favour of the dynamical theory. On this view, the large expansion in volume caused by a non-polar double bond indicates that when four shared electrons move in orbits around or between the

two atoms which share them the mutual interactions of the electrons thus crowded together lead to a looser structure of the molecule as a whole.

It should be emphasised here that, with this exception, none of the results of the Lewis-Langmuir theory discussed in the present paper is concerned with the assumption of a cubical atom or of a statical theory of atomic structure. All the deductions with regard to valency follow from two postulates: (*a*) that a covalency consists of two shared electrons, and (*b*) that the maximum number of electrons in the outer shell of any atom is eight. The latter assumption is limited to the first two periods of the periodic table by Langmuir, who, for elements of higher atomic number, postulates the existence of a greater number of electrons in the outer shell. This view has been modified by Bury (*J. Amer. Chem. Soc.*, 1921, **43**, 1602), who retains the outer shell of eight for all the inert gases, whilst Bohr's theory of atomic structure ("The Theory of Spectra and Atomic Structure," Cambridge University Press, 1922) retains eight electrons of greatest total quantum number, which may be regarded as valency electrons.

In this connexion the recent measurements of von Wartenberg (*Annalen*, 1924, **440**, 97) of the surface tension and density of osmium tetroxide are of considerable interest, as they provide an experimental test of the truth of the octet theory for an element of high atomic number. From these data, the parachor for osmium tetroxide is 154·0. On the assumption that the oxygens are held by four semipolar double bonds giving an outer shell of eight electrons, the parachor for osmium is 80·4; if the osmium atom in this compound has an outer shell of sixteen electrons, and four non-polar double bonds are present, then the parachor for osmium becomes — 18·8. Although there are no further data on osmium compounds available from which an independent value of the parachor can be obtained, it will be seen from the rough values for neighbouring elements given below that the value $Os = 80$ falls into place in the series which exhibits a minimum at gold. Hence it appears probable that osmium tetroxide has the structure $Os(=O)_4$ and that the octet rule may hold for elements of high atomic number as well as for the first two periods of the table.

Element	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi
Atomic number	76	77	78	79	80	81	82	83
Parachor	80	—	68	54	70	—	90	92
Observer	—	—	Q.	Hey.	H.	—	H.	H.

In most of his formulæ Langmuir assumes wherever possible the formation of complete octets; in later theories (Latimer and Rodebush, *J. Amer. Chem. Soc.*, 1920, **42**, 1419), the existence of

sextets is postulated in certain cases. In particular, Lowry (J., 1923, **123**, 822) has suggested that most double bonds are semi-polar and states that " a double bond in organic chemistry usually reacts as if it contained one covalency and one electrovalency." This view has been criticised on stereochemical grounds (Sugden, *ibid.*, p. 1861; Farmer, *ibid.*, p. 2531) and, so far as the normal state of the molecule is concerned, it seems necessary to retain the conception of the non-polar double bond to account for the existence of geometrical isomerides. We have now, in the parachor, a method of determining experimentally what type of linking is present in a particular molecule, and the remainder of the present paper will be devoted to the discussion of the constitution of a number of unsaturated compounds of carbon, nitrogen, phosphorus, and sulphur for which experimental values of this constant are available.

(3) *Carbon Compounds.*

The non-polar double bond contributing 23·2 units to the molecular parachor appears, so far, to be the only type of double linking in which the carbon atom takes part. It has been found in more than one hundred carbon compounds including hydrocarbons, aldehydes, ketones, and esters. In particular, it may be mentioned that five pairs of geometrical isomerides recently examined in this laboratory have all been found to possess this type of linking.*

The case of the carbonates is of special interest. Langmuir gives the usual formula $(RO)_2C{=}O$ and points out that carbonates are not isomorphous with sulphites, which, on Lowry's method of formulation, have the structure $(RO)_2S{\rightleftharpoons}O$. On the other hand, Lowry suggests that the stability of oxyacids depends upon the presence of a positively charged nuclear atom and writes the carbonate ion $\overset{-}{O}{-}\overset{+}{C}\begin{matrix}\overset{-}{O}\\ \\ O\end{matrix}$. We have therefore measured the surface tension and density of two esters of carbonic acid with the following results :

		[*P*] calc.	
	[*P*] obs.	Non-polar.	Semipolar.
Diethyl carbonate	277·4	278·2	253·4
Diphenyl carbonate	467·4	468·0	443·2

It is evident that these compounds contain a non-polar double bond.

(4) *Nitrogen Compounds.*

The structure of nitrous acid presents the same ambiguity as that of carbonic acid. Langmuir gives the formula $RON{=}O$, whilst

* The data for these substances will be presented in a later paper.

Lowry assumes that a semipolar double bond is present and writes the nitrite ion $\bar{O}—\overset{+}{N}—\bar{O}$. We have therefore examined two esters of nitrous acid; it will be seen from the values found for the parachor that Langmuir's formula is correct and that the esters of nitrous acid, like those of carbonic acid, do not contain a positively charged nuclear atom.

		[*P*] calc.	
	[*P*] obs.	Non-polar.	Semipolar.
n-Butyl nitrite	251·8	248·8	224·0
*iso*Amyl nitrite	287·4	287·8	263·0

The existence of two types of double bond gives no fewer than four possible formulæ for the nitro-group. These formulæ together with the corresponding values of the parachor for the group NO_2 are given below. Formula (VI) is of course excluded by the octet


98·9
(VI.)


74·1
(VII.)


49·3
(VIII.)

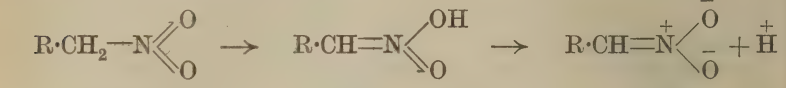

69·5
(IX.)

theory, and Langmuir adopted (VII) for this group, whilst Latimer and Rodebush and Lowry give the symmetrical formula (VIII). In the first paper on the parachor, it was pointed out that the experimental figures for this group were much smaller than would be expected for (VI) and it was assumed that the nitro-group possessed the alternative cyclic structure (IX). If this view is accepted, then from the experimental figures for nitro-compounds the constant for a three-membered ring is 21·5. An investigation of derivatives of *cyclo*propane and of ethylene oxide is now in progress, and the results so far obtained indicate that this value is too high and that the constant for a three-membered ring is approximately 17 units; this figure has been used in calculating the parachor given under (IX). The experimental data for nitro-compounds are tabulated below; the mean value of 74·2 is very close to the figure calculated for (VII), and (VI) and (VIII) are certainly excluded. The difference between (VII) and (IX) is not very large; the balance of evidence

Substance.	Formula.	Observer.	[*P*] obs.	Σ[*P*].	NO_2
Nitrogen peroxide	$NO_2 \cdot NO_2$	R. & S.	144·4	0	72·2
Nitromethane	$CH_3 \cdot NO_2$	M. & S.	132·0	56·1	75·9
		H. C. & R.	132·1	,,	76·0
Ethyl nitrate	$C_2H_5 \cdot O \cdot NO_2$	M. & S.	189·6	115·1	74·5
Nitrobenzene	$C_6H_5 \cdot NO_2$	S.	264·5	190·0	74·5
p-Nitrotoluene	$C_7H_7 \cdot NO_2$	,,	302·8	229·0	73·8
p-Nitrochlorobenzene ...	$C_6H_4Cl \cdot NO_2$	,,	300·0	227·2	72·8
					Mean 74·2

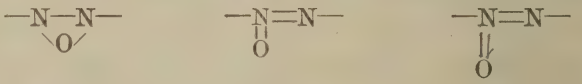
is in favour of (VII), although (IX) cannot be entirely excluded until the constant for a three-membered ring has been investigated more

fully. On chemical grounds, the Langmuir formula (VII) is to be preferred to the cyclic formula, as it suggests an explanation of the production of an *aci*-form from primary and secondary nitroparaffins as indicated in formulæ (X), (XI), and (XII). On this view the ion of the ψ-acid has the symmetrical formula (XII) suggested by Lowry, whilst the original nitro-compound contains only one semipolar double bond.



(X.) (XI.) (XII.)

Azoxy-compounds were at one time supposed to have the structure shown in (XIII). The existence of pairs of isomerides of a number of unsymmetrical azoxy-compounds (Angeli, *Ahrens Vort.*, 1913, **19**, 447) has led to the adoption of formula (XIV), which is, however, impossible on the octet theory, since the nitrogen atom is quinquecovalent. One of the double bonds must be semipolar and from electrochemical considerations and from the fact that azoxy-compounds are readily formed by the oxidation of azo-compounds it appears probable that this is the linking between nitrogen and



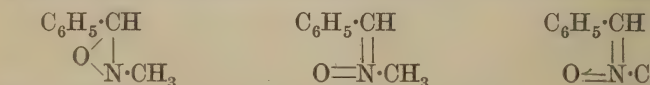
62·0 91·2 66·7
(XIII.) (XIV.) (XV.)

oxygen as shown in (XV). We have examined azoxybenzene and *o*-azoxytoluene with the following results :

	[*P*] obs.	Σ[*P*].	N_2O.
Azoxybenzene	444·7	380·0	64·7
o-Azoxytoluene	528·6	458·0	70·6

If Angeli's evidence for excluding formula (XIII) is accepted, these results give a satisfactory confirmation of (XV).

We are indebted to Dr. O. L. Brady for the loan of specimens of the *N*- and *O*-methyl ethers of benz*anti*aldoxime, the measurement of which has given the following results : *O*-Methyl ether, [*P*] obs. = 324·2 ; *N*-methyl ether, [*P*] obs. = 325·9. The *O*-ether must have the structure $C_6H_5{\cdot}CH{:}N{\cdot}O{\cdot}CH_3$, for which [*P*] calc. = 323·7, in good agreement with the observed value. For the *N*-ether the structures indicated in formulæ (XVI), (XVII), and (XVIII) are



317·5 346·9 321·2
(XVI.) (XVII.) (XVIII.)

possible. Here, again, the parachor confirms the octet theory in excluding formulæ such as (XVII) in which nitrogen is quinquecovalent. The observed figure, whilst rather high, is in favour of the modified nitrone structure (XVIII) with a semipolar double bond between nitrogen and oxygen.

The investigation of other types of quinquevalent nitrogen compounds will obviously be of considerable interest, and we hope to extend our work in this direction in the near future. For the three types so far examined, namely, nitro-compounds, azoxy-compounds, and *N*-oximino-ethers, the parachor confirms completely Langmuir's contention that the maximum covalency of nitrogen is four, the fifth valency, as pointed out by Lowry, being always an electrovalency.

(5) *Phosphorus Compounds.*

The following table contains the data from which the parachor for phosphorus has been deduced and does not call for further comment :

Substance.	Formula.	Observer.	$[P]$ obs.	$\Sigma[P]$.	Phosphorus
Phosphorus trichloride	PCl_3	M. & D.	199·0	162·9	36·1
		R. & S.	201·1	,,	38·2
Phosphorus tribromide...	PBr_3	S. R. & W.	242·9	204·0	38·9
Triphenylphosphine	$P(C_6H_5)_3$	W. & S.	607·7	570·0	37·7
					Mean 37·7

Data for phosphorus oxychloride and for two esters of phosphoric acid are contained in Table II. In accordance with the octet theory the double bond in these compounds is of the semipolar type.

(6) *Sulphur Compounds.*

The following table contains the data from which the parachor for sulphur has been calculated :

Substance.	Formula.	Observer.	$[P]$ obs.	$\Sigma[P]$.	Sulphur
Sulphur monochloride ...	S—Cl | S—Cl	R. & S.	205·1	108·6	48·2
Carbon disulphide	S=C=S	,,	144·7	51·2	46·8
		M. & T. M. & D.	143·6	,,	46·2
		H. C. & R.	142·9	,,	45·9
Ethyl mercaptan	C_2H_5·SH	M. & C.	162·9	112·2	50·7
Phenyl mercaptan.....	C_6H_5·SH	W. & S.	257·5	207·1	50·4
		M. & C.	256·4	,,	49·3
					Mean 48·2

The data for the acid chlorides and esters of sulphurous and sulphuric acids are contained in Table II; in accordance with the requirements of the octet theory these compounds all contain semipolar double bonds.

Data for a few thiocyanates and thiocarbimides are available and

present some points of interest. The table below shows that the double and triple bonds in these compounds are all of the non-polar type, since the values of $[P]$ calc. obtained on this assumption are in good agreement with the observed figures. The double bonds in carbon disulphide also are non-polar, hence the absence of such bonds in sulphites and sulphates cannot be ascribed to an intrinsic property of the sulphur atom which prevents the formation of normal linkings.

Substance.	Formula.	Observer.	$[P]$ obs.	$[P]$ calc.
Methyl thiocyanate	$CH_3{\cdot}S{\cdot}C{:}N$	Sch.	168·6	168·2
Ethyl thiocyanate	$C_2H_5{\cdot}S{\cdot}C{:}N$	R. & S.	210·7	207·2
		M. & C.	209·1	,,
Ethylthiocarbimide	$C_2H_5{\cdot}N{:}C{:}S$	,,	211·7	207·0
Allylthiocarbimide	$C_3H_5{\cdot}N{:}C{:}S$	,,	232·4	235·0
Phenylthiocarbimide	$C_6H_5{\cdot}N{:}C{:}S$	,,	304·1	301·9

Ethyl thiocyanate and ethylthiocarbimide have almost exactly the same parachor. This is further evidence for the value 46·6 for the triple bond (deduced from nitriles and acetylene derivatives), which is almost exactly twice the constant for a non-polar double bond (23·2). This suggests that each covalency in a multiple bond adds 23·2 units except the first one, which has no effect on the parachor.

In conclusion, it should be stated that in the present paper we are considering only the structure of the molecule in the " resting " state, whilst some of the formulæ discussed above (particularly those of Lowry) are intended to refer to the " reactive " condition. The arrangement of the atoms in the molecule in the " resting " state expressed in the structural formula is fundamental, not only for stereochemistry and for the discussion of physical properties, but as a basis for the consideration of the structure of the molecule in the " reactive " state. The structure of the activated molecule, if it differs perceptibly from that of the inactive molecule, must be simply related to it. We have shown in the present paper that whilst semipolar double bonds do occur in certain compounds they are not found in the non-activated molecules of carbon compounds generally. Lowry's hypothesis concerning carbon compounds may therefore be taken to mean that the activation of such compounds consists in the transference of an electron whereby a non-polar double bond is converted into one of the semipolar type. This view does give a simple connexion between the structures in the activated and non-activated states; it is beyond the scope of the present paper to discuss whether this hypothesis gives a satisfactory picture of the nature of the change involved in the process of activation. So far as the non-activated molecules are concerned, one general rule holds. Semipolar double bonds are only formed when each

atom except hydrogen has attained a complete octet and when the formation of a non-polar double bond would cause one or other of the atoms concerned to be associated with more than eight electrons, or, in other words, to have a covalency greater than four.

Summary.

(1) By means of the parachor the existence of two types of double bond has been demonstrated experimentally.

(2) These are identified as the non-polar and semipolar double bonds predicted by the octet theory as developed by Lewis, Langmuir, and Lowry.

(3) The nature of the double linking in a number of compounds of carbon, nitrogen, phosphorus, and sulphur has been investigated. In all the cases so far examined, semipolar double bonds are formed only when each atom, except hydrogen, has attained a complete octet. The octet is never exceeded and semipolar bonds are not found when their existence would necessitate the presence of a sextet around one or other of the atoms concerned. Sextets must be present in a few cases, as in the ion of triphenylmethyl chloride, but such structures are apparently rare.

(4) There is some evidence that the octet rule is not restricted to elements of the first two periods of the periodic table, but that it may hold for elements of higher atomic number.

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Experimental.

New measurements have been made of the surface tension and density of sixteen substances, the former by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27) and densities by means of the U-shaped pyknometer described in

the second of these papers. Three bubblers were used, the constants for which are given below:

App.	8b.	8c.	4d.
r_2	0·206	0·206	0·139 cm.
A	0·003730	0·005622	0·007767

In the tables below, the first column gives the apparatus used and the second column the temperature. The thermometers used were compared with a reference standard calibrated at the National Physical Laboratory and the observations are corrected for exposed stem. The difference of the pressures (expressed in dynes/cm.^{2}) required to liberate bubbles from the two tubes of the bubbler is given under P, D is the density of the liquid in g./c.c., and ϕ a correction factor calculated by the formula $\phi = 1 + 0{\cdot}69r_2gD/P$, where r_2 is the radius of the wide tube in cm. and $g = 981$ cm./sec.^{2}. γ is the surface tension in dynes/cm. calculated by the equation $\gamma = AP\phi$, where A is the apparatus constant determined by experiments with benzene. The parachor in the last column is then obtained by the expression $[P] = \gamma^{1/4}M/(D - d)$, where M is the molecular weight and d the density of the vapour in g./c.c. In most cases d is very small compared with D and can be neglected except at temperatures approaching the boiling point. A method of calculating approximate values of the vapour density is given as an appendix to this paper, and has been used in those cases in which $D - d$ has been placed at the head of column 4 in the tables below.

Ethyl carbonate was twice fractionally distilled; the portion used boiled at 125·2—125·8° (corr.)/756 mm. Densities determined: $D_{4°}^{13°}$ 0·974, $D_{4°}^{26°}$ 0·959, $D_{4°}^{42°}$ 0·941, $D_{4°}^{56·5°}$ 0·925; whence $D_{4°}^{t°} = 0{\cdot}988—0{\cdot}00113t$. Molecular weight 118·1.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
4d	13°	3425	0·973	1·0268	27·30	277·5
,,	33	3112	0·951	1·0288	24·86	277·3
,,	43·5	2965	0·939	1·0298	23·71	277·5
,,	65·5	2640	0·914	1·0326	21·17	277·2
						Mean 277·4

Phenyl carbonate was recrystallised from absolute alcohol and melted sharply at 79·5° (corr.). Densities determined: $D_{4°}^{87°}$ 1·1215, $D_{4°}^{111°}$ 1·0997, $D_{4°}^{145°}$ 1·0690; whence $D_{4°}^{t°} = 1{\cdot}2002—0{\cdot}000905t$. Molecular weight 214·1.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
4d	101°	4308	1·1089	1·0242	34·28	467·2
,,	120·5	4041	1·0912	1·0254	32·19	467·3
,,	139	3815	1·0744	1·0264	30·41	467·8
						Mean 467·4

n-*Butyl nitrite* was prepared from *n*-butyl alcohol and repeatedly fractionated. The specimen used boiled at 75—76° (corr.)/768 mm.

Densities determined : $D_4^{11°}$ 0·8928, $D_4^{26°}$ 0·8756, $D_4^{44·5°}$ 0·8534; whence $D_4^{t°} = 0·9059—0·001176t$. Molecular weight 103·1.

App.	t.	P.	$D - d$.	ϕ.	γ.	Parachor.
4d	13°	2781	0·8901	1·0301	22·25	251·5
,,	28·5	2555	0·8716	1·0321	20·48	251·6
,,	42·5	2380	0·8547	1·0338	19·12	252·1
,,	56·5	2184	0·8375	1·0361	17·58	252·0
					Mean	251·8

iso*Amyl nitrite* was prepared from Kahlbaum's *iso*amyl alcohol and was repeatedly fractionated. The specimen used boiled at 98·5—99·5° (corr.)/768 mm. Densities determined : $D_4^{13·5°}$ 0·885, $D_4^{24·5°}$ 0·864, $D_4^{74°}$ 0·820; whence $D_4^{t°} = 0·900—0·00108t$.

App.	t.	P.	$D - d$.	ϕ.	γ.	Parachor.
4d	14°	2821	0·885	1·0295	22·04	286·7
,,	35	2539	0·862	1·0320	20·35	288·5
,,	56	2247	0·839	1·0350	18·06	287·7
,,	73	2019	0·820	1·0380	16·28	286·8
					Mean	287·4

Azoxybenzene was recrystallised from ligroin and melted at 35·0—35·5° (corr.). Densities determined : $D_4^{14°}$ 1·150, $D_4^{68·5°}$ 1·132, $D_4^{78·5°}$ 1·122, $D_4^{91·5°}$ 1·109; whence $D_4^{t°} = 1·189—0·000864t$. Molecular weight 198·2.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
8b	51°	11460	1·145	1·0140	43·34	444·0
,,	66·5	10945	1·132	1·0144	41·42	444·0
,,	77·5	10637	1·122	1·0147	40·26	444·8
,,	89	10356	1·112	1·0150	39·17	445·8
					Mean	444·7

o-*Azoxytoluene* was recrystallised from ligroin and melted at 58—59° (corr.). Densities determined : $D_4^{74°}$ 1·0768, $D_4^{83°}$ 1·0698, $D_4^{91°}$ 1·0637, $D_4^{125·5°}$ 1·0369, $D_4^{139°}$ 1·0248; whence $D_4^{t°} = 1·1353—0·000790t$. Molecular weight 226·2.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
8b	69·5°	10686	1·0804	1·0141	40·41	527·9
,,	78·5	10412	1·0733	1·0144	39·39	528·0
,,	90·5	10130	1·0638	1·0146	38·33	529·0
,,	101	9839	1·0555	1·0150	37·25	529·4
					Mean	528·6

O-*Methyl ether* of benz*anti*aldoxime. The specimen supplied by Dr. O. L. Brady was distilled immediately before measurement and boiled at 197—199° (corr.)/762 mm. Densities determined : $D_4^{13·5°}$ 1·0325, $D_4^{30·5°}$ 1·0165, $D_4^{51·5°}$ 0·9967, $D_4^{72°}$ 0·9757; whence $D_4^{t°} = 1·0465—0·000976t$. Molecular weight 135·1.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
4d	16·5°	4670	1·0304	1·0208	37·03	323·4
,,	33·5	4399	1·0138	1·0217	34·92	324·3
,,	55·5	4052	0·9923	1·0230	32·20	324·4
,,	73	3788	0·9753	1·0242	30·13	324·6
					Mean	324·2

N-*Methyl ether* of benz*anti*aldoxime. The specimen supplied by Dr. O. L. Brady melted sharply at 84° (corr.). Densities determined : $D_{4°}^{103°}$ 1·0505, $D_{4°}^{120°}$ 1·0357, $D_{4°}^{135·5°}$ 1·0236, $D_{4°}^{151°}$ 1·0117; whence $D_{4°}^{t°} = 1·1333—0·000808t$. Molecular weight 135·1.

App.	*t.*	*P.*	*D.*	ϕ.	γ.	Parachor.
4d	100°	5171	1·0525	1·0192	40·93	324·7
,,	122	4875	1·0347	1·0200	38·62	325·4
,,	141	4641	1·0194	1·0207	36·80	326·4
,,	163	4352	1·0016	1·0216	34·53	327·0
						Mean 325·9

Phosphorus tribromide was repeatedly fractionated first at ordinary pressure and finally under reduced pressure. The specimen used boiled at 66·5° (corr.)/20 mm. and at 176—177° (corr.)/772 mm. Some difficulty was experienced in measuring the surface tension of this substance owing to the presence of an orange-coloured impurity which separated slowly and blocked the capillary. This was not removed by repeated distillations at atmospheric pressure, but was left behind when the substance was distilled at 20 mm. A drying tube, 60 cm. long, filled with phosphorus pentoxide, was fitted above the bubbler to dry the incoming air. Densities determined : $D_{4°}^{15°}$ 2·904, $D_{4°}^{33·5°}$ 2·860, $D_{4°}^{52°}$ 2·813, $D_{4°}^{70·5°}$ 2·768; whence $D_{4°}^{t°} = 2·942—0·00247t$. Molecular weight 270·8.

App.	*t.*	*P.*	*D.*	ϕ.	γ.	Parachor.
4d	24°	5630	2·883	1·048	45·8	244·4
,,	33	5410	2·861	1·050	44·1	244·0
,,	59·5	4680	2·795	1·056	38·4	241·2
,,	72	4520	2·764	1·058	37·1	242·0
						Mean 242·9

Phosphorus oxychloride was twice distilled; the fraction used boiled at 108·6—108·8° (corr.)/769 mm. Densities determined : $D_{4°}^{14·5°}$ 1·691, $D_{4°}^{31·5°}$ 1·659, $D_{4°}^{49·5°}$ 1·625; whence $D_{4°}^{t°} = 1·718—0·00188t$. Molecular weight 153·4.

App.	*t.*	*P.*	*D.*	ϕ.	γ.	Parachor.
8c	15°	5595	1·690	1·0421	32·77	217·1
,,	49	4819	1·626	1·0471	28·36	217·7
,,	65	4504	1·596	1·0494	26·57	218·1
						Mean 217·6

Triethyl phosphate was prepared by the method of Limpricht (*Annalen*, 1865, **134**, 347) and was fractionated twice under diminished pressure. The specimen used boiled at 108° (corr.)/25 mm. and, with slight decomposition, at 216° (corr.)/770 mm. Densities determined : $D_{4°}^{15°}$ 1·0794, $D_{4°}^{38°}$ 1·0551, $D_{4°}^{52·5°}$ 1·0395, $D_{4°}^{67°}$ 1·0257, $D_{4°}^{83°}$ 1·0093; whence $D_{4°}^{t°} = 1·0943—0·001028t$. Molecular weight 182·2.

App.	$t.$	$P.$	$D.$	$\phi.$	$\gamma.$	Parachor.
8c	15·5°	5294	1·0784	1·0284	30·61	397·7
,,	38·5	4887	1·0547	1·0301	28·30	398·4
,,	69·5	4383	1·0229	1·0325	25·44	400·1
,,	87·5	4067	1·0044	1·0344	23·65	400·1
						Mean 399·1

Triphenyl phosphate was recrystallised from a mixture of absolute alcohol and ligroin and melted sharply at 50° (corr.). Densities determined: D_4^{58} 1·2055, $D_4^{68\cdot5°}$ 1·1970, $D_4^{79\cdot5°}$ 1·1883, $D_4^{89°}$ 1·1803; whence $D_4^{t°} = 1·2523—0·000807t$. Molecular weight 326·2.

App.	$t.$	$P.$	$D.$	$\phi.$	$\gamma.$	Parachor.
4d	65·5°	5118	1·1994	1·0221	40·63	686·5
,,	74	4991	1·1926	1·0225	39·64	686·3
,,	84	4872	1·1845	1·0229	38·71	686·8
						Mean 686·5

Thionyl chloride was repeatedly fractionated; the specimen used boiled at 76·9—77·1° (corr.)/772 mm. Densities determined: $D_4^{14\cdot5°}$ 1·656, $D_4^{32°}$ 1·622, $D_4^{48°}$ 1·593; whence $D_4^{t°} = 1·683—0·00188t$. Molecular weight 119·0.

App.	$t.$	$P.$	$D - d.$	$\phi.$	$\gamma.$	Parachor.
8c	18	5820	1·649	1·0395	34·01	174·3
,,	37	5375	1·613	1·0418	31·48	174·8
,,	51	4992	1·587	1·0443	29·31	174·4
						Mean 174·5

Sulphuryl chloride was prepared by boiling chlorosulphonic acid with a little mercuric sulphate and was repeatedly fractionated. The specimen used boiled at 70·0—70·2° (corr.)/772 mm. For the surface tension measurements the incoming air was dried over phosphorus pentoxide. Densities determined: $D_4^{12°}$ 1·700, $D_4^{25°}$ 1·671, $D_4^{38\cdot5°}$ 1·640; whence $D_4^{t°} = 1·727—0·00227t$. Molecular weight = 135·0.

App.	$t.$	$P.$	$D - d.$	$\phi.$	$\gamma.$	Parachor.
4d	13°	4380	1·696	1·0364	35·26	193·9
,,	23·5	4081	1·673	1·0386	32·92	193·3
,,	47·5	3504	1·617	1·0434	28·40	192·8
						Mean 193·3

Dimethyl sulphate. The commercial product was distilled once under reduced pressure and fractionated at atmospheric pressure. The specimen used boiled at 187·5° (corr.)/769 mm. Densities determined: $D_4^{16\cdot5°}$ 1·3367, $D_4^{38°}$ 1·3093, $D_4^{59\cdot5°}$ 1·2820, $D_4^{82\cdot5°}$ 1·2533; whence $D_4^{t°} = 1·3575—0·001265t$. Molecular weight 126·1.

App.	$t.$	$P.$	$D.$	$\phi.$	$\gamma.$	Parachor.
4d	18°	5038	1·3347	1·0249	40·12	237·7
,,	36·5	4738	1·3113	1·0260	37·76	238·3
,,	55	4444	1·2879	1·0273	35·46	238·8
,,	74·5	4163	1·2632	1·0285	33·25	239·6
,,	93	3879	1·2399	1·0301	31·03	240·0
						Mean 238·9

Diethyl sulphate. The commercial product was twice distilled under diminished pressure; the specimen used boiled at 110°

(corr.)/30 mm. Densities determined: $D_4^{12°}$ 1·197, $D_4^{20·5°}$ 1·175, $D_4^{50·5°}$ 1·153, $D_4^{67°}$ 1·135; whence $D_4^{t°} = 1·210—0·00112t$. Molecular weight 154·1.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
4d	13°	4344	1·195	1·0259	34·61	312·7
,,	32·5	4080	1·174	1·0271	32·54	313·5
,,	48	3866	1·156	1·0281	30·86	314·2
,,	70	3576	1·132	1·0298	28·60	314·8
						Mean 313·8

Appendix.

Calculation of Vapour Density in the Neighbourhood of the Boiling Point.—The expression for the parachor involves the quantity $D - d$ and whilst the vapour density, d, is small compared with D in most cases, it becomes sufficiently large to affect the value of the parachor at temperatures approaching the boiling point. The value of d can, however, be calculated in the following manner with sufficient accuracy, since it only enters into the expression for the parachor as a small correction term.

If it is assumed that the gas laws hold for the vapour at the boiling point, then $d_b = 0·0122M/T_b$, where d_b is the vapour density at the boiling point T_b on the absolute scale at 760 mm., whilst M is the molecular weight. For lower temperatures, the variation of the vapour density is expressed with sufficient accuracy by the expression $\log_{10}d/d_b = 5(T/T_b - 1)$, where d is the vapour density at an absolute temperature, T. The accuracy with which this empirical expression can be used to calculate the vapour density is shown by the examples below. The values of d obs. are those given by Young (*Proc. Roy. Soc. Dublin*, 1910, **12**, 374).

Benzene: $T_b = 353$, $d_b = 0·0027$.

t.	d calc.	d obs.	Diff.
80°	0·0027	0·0027	±0·0000
60	0·0014	0·0015	−0·0001
40	0·0007	0·0008	−0·0001
20	0·0004	0·0004	±0·0000

Chlorobenzene: $T_b = 405$, $d_b = 0·0034$.

t.	d calc.	d obs.	Diff.
120°	0·0024	0·0026	−0·0002
100	0·0014	0·0014	±0·0000
80	0·0008	0·0008	±0·0000
60	0·0004	0·0002	+0·0002

Diethyl ether: $T_b = 308$, $d_b = 0·0029$.

t.	d calc.	d obs.	Diff.
30°	0·0024	0·0027	−0·0003
20	0·0016	0·0019	−0·0003
10	0·0012	0·0013	−0·0001
0	0·0008	0·0008	±0·0000

Ethyl acetate: $T_b = 350$, $d_b = 0·0031$.

t.	d calc.	d obs.	Diff.
60°	0·0016	0·0018	−0·0002
40	0·0009	0·0008	+0·0001
20	0·0003	0·0003	±0·0000

One of us (S. S.) is indebted to the Research Fund Committee of the Society for a grant which has partly defrayed the cost of this investigation.

Birkbeck College (University of London),
Fetter Lane, E.C. 4. [*Received, April 17th*, 1925.]

CCIV.—*The System Chromium Trioxide–Boric Acid–Water.*

By Lionel Felix Gilbert.

This investigation was undertaken in continuation of previous work on the interaction of chromic acid with other acids (Gilbert, Buckley, and Masson, J., 1922, **121**, 1935; Mumford and Gilbert, J., 1923, **123**, 471).

The general experimental method was similar to that previously described (*loc. cit.*). The reaction tubes were partly filled with chromic acid solutions of different concentrations and with approximately known amounts of (ortho-) boric acid. The temperatures were again 25° and 45°.

Chromic acid was estimated iodometrically; total acidity was determined by titration of another sample with barium hydroxide, mannitol being added when the end-point, indicated by phenolphthalein, was near. As the commercial mannitol used had a slightly acid reaction, it was found convenient to make up a saturated stock solution in water and to neutralise from time to time with barium hydroxide. A few c.c. of the saturated solution were sufficient for each titration. Baryta was run into each suitably diluted mixture till a definite pink colour persisted for 3 minutes (compare Kolthoff, *Chem. Weekblad*, 1922, **19**, 449). This end-point is, however, sometimes difficult to determine accurately.

The results obtained are shown in Tables I and II, boric acid

Table I.

Compositions (g. per 100 g.) and densities at 25°.

Liquid phase.			Wet solid.	
$d_4^{25°}$.	CrO_3.	B_2O_3.	CrO_3.	B_2O_3.
1·699	62·40	0·10	32·38	26·09
1·657	59·90	0·16	35·82	22·36
	53·72	0·28		
	49·75	0·42	45·39	5·28
1·420	43·80	0·65	24·42	24·89
	37·89	0·92	21·12	25·11
1·296	33·05	1·02	17·94	26·07
1·212	24·31	1·35	9·02	35·72
1·156	18·07	1·58	9·30	28·52
1·086	9·42	2·28	5·19	27·07
1·052	4·90	2·79	2·50	31·01

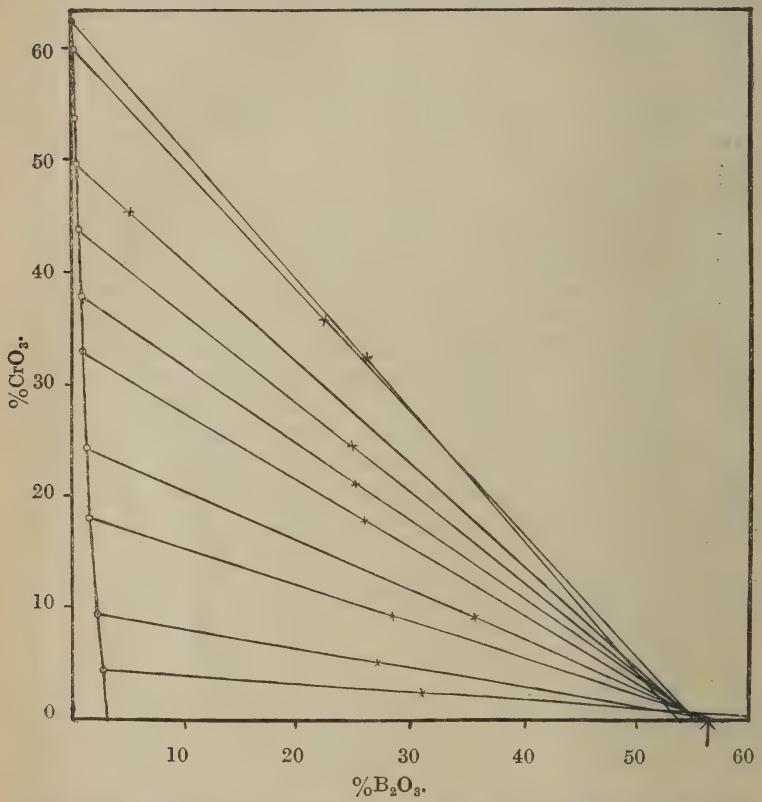
Table II.

Compositions (g. per 100 g.) and densities at 45°.

Liquid phase.			Wet solid.	
$d_4^{45°}$.	CrO_3.	B_2O_3.	CrO_3.	B_2O_3.
1·674	61·56	0·90	39·31	20·84
1·612	58·10	0·92	33·96	23·91
1·603	57·50	0·87	29·78	27·42
1·603	57·34	1·12	32·71	24·43
1·528	53·80	0·85	24·28	29·88
1·219	25·60	2·33	11·58	32·10
1·038	2·40	4·76	0·93	36·53

being calculated as B_2O_3; the data of Table I are also shown graphically in the figure, in which the value shown for the solubility of boron trioxide in water at 25° (3·1% B_2O_3) has been calculated from Seidell's tables. It will be observed that the productions of the tie-lines connecting liquids with corresponding wet solids pass very closely to the point representing the composition of boric

acid (56·3% B_2O_3, marked by an arrow on the diagram). The same occurs when the data for 45° are plotted. Apparent irregularities at 45° in the boron trioxide content of solutions containing much chromium trioxide may be ascribed to analytical errors, especially as the end-point in the total acidity determination is not sharp, and the small amounts of boron trioxide are determined by



The solubility of boric acid in aqueous solutions of chromic acid at 25°.

difference. For these reasons no great accuracy is claimed for the boron trioxide determinations, but from the behaviour of the tie-lines there seems no doubt that the solid phase is always boric acid. The shape of the curve appears to indicate that the depression of solubility of boric acid as the concentration of chromic acid is raised is due chiefly to common ion (hydrogen) action.

THE WILLIAM RAMSAY INORGANIC AND PHYSICAL CHEMISTRY LABORATORIES,
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[*Received, May* 21*st*, 1925.]

CCV.—*The Dissociation Constants of Selenious Acid.*

By James Stuart Willcox and Edmund Brydges Rudhall Prideaux.

The first dissociation constant of selenious acid as determined by Ostwald ("Allgemeine Chemie," 1893) is $1{\cdot}59 \times 10^{-3}$ (conductivity method). The first and second constants as determined by Blanc (*J. Chim. phys.*, 1920, **18**, 39) are $2{\cdot}7 \times 10^{-3}$ and $5{\cdot}1 \times 10^{-8}$. Blanc, who stated his results with considerable reserve, appears to have used the following method. 0·595*N*-Sodium hydroxide was added, 0·1 c.c. at a time, to 0·0108*N*-selenious acid, and from the results obtained a conductivity–neutralisation curve was plotted, the rectilinear branches of which were produced in the usual manner to give the points of intersection corresponding to $NaHSeO_3$ and Na_2SeO_3. Solutions of the two salts prepared in accordance with these results were then treated with congo-red, phenolphthalein, or α-naphtholbenzoïn and matched against buffer solutions of acetate and phosphate. These indicators were admittedly unsatisfactory; at the second point, $p_H = 9{\cdot}7$, phenolphthalein was at the limit of its change, and the colour change of naphtholbenzoïn was not a pronounced one. Owing to the shape of the curve at these points, however, the accuracy in the determination of p_H was probably sufficient. We consider that a more serious source of error is the difficulty of finding the p_H points of inflection on the neutralisation–conductivity curve and of reproducing the correct stoicheiometrical proportions of acid and alkali with sufficient accuracy. For example, whilst 0·1 c.c. of alkali of the concentration employed by Blanc neutralises 6% of the acid, a change of 1% in the amount neutralised corresponds, from our curve, with a change of 1·0 in p_H value. We have therefore redetermined the constants with the aid of several indicators, including some of the modern ones, and at those stages of neutralisation at which the solutions are well buffered, and therefore not unduly sensitive to small errors in the addition of alkali.

Experimental.

A solution of selenium dioxide (prepared according to the usual method) in alcohol was filtered, and evaporated to dryness on the water-bath; the residue was recrystallised several times from hot water. To 20 c.c. of a 0·05*M*-solution of this selenious acid (factor 0·97, found by analysis, the acid being converted into and weighed as selenium) were added measured volumes of 0·189*N*-sodium hydroxide, free from carbonate, in the presence of suitable indicators. The colours were matched, in Nessler glasses, against

those of solutions obtained by the addition of the same alkali to 20 c.c. of the British Drug Houses universal indicator (J., 1924, **125**, 427) containing the same number of drops of indicator, and hence the hydrion concentrations corresponding to each 3% of acid neutralised were obtained.

Calculation of K_1 *and* K_2.—In the following tables x is the number of c.c. of alkali added to 20 c.c. of the selenious acid solution. The percentage of acid neutralised is calculated from the value of x, and the total concentration, c, of the acid is $0{\cdot}97/(20 + x)$. The concentration of the sodium salt, [NaHA], and of the anion derived from this, is $0{\cdot}189x/(20 + x)$. Individual values of h + [NaHA] and $c - (h + [\mathrm{NaHA}])$ introduced into the equation

$$K_1 = h(h + [\mathrm{NaHA}])/\{c - (h + [\mathrm{NaHA}])\} \quad . \quad . \quad (a)$$

give the values of K_1 up to $p_{\mathrm{H}} = 3{\cdot}9$; the results marked * in the tables have been used. For values of p_{H} a little greater than 3 up to 4, equation (1) (J., 1924, **125**, 427), which does not take account of the total concentration, may be used, terms containing K_2 being omitted; *i.e.*,

$$K_1 = Rh/(1 - R) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where R = equivalents of alkali added to 1 mol. of acid = % acid neutralised — 50. For values of p_{H} from 6·0 upwards, K_2 is calculated from the equation

$$K_2 = h(R - 1)/(2 - R) \quad . \quad . \quad . \quad . \quad (2)$$

The figures marked † in the tables have been introduced into equation (1), those marked ‡ into equation (2).

Thymol-blue.

x	0·5	1·0	1·5	2·0	2·55	3·0	3·57	4·0
% acid neutr.	5	9·8	14·5	19·5	24·9	29·2	35	39
p_{H}	2·2*	2·28*	2·35*	2·4*	2·45*	2·49*	2·65*	2·82*

In the following tables the percentage of acid neutralised is equal to $10x - 1$.

B.D.H. universal indicator.

x ..... =	4·7	5·0	5·1	5·2	5·3	5·4	5·5
p_{H} ..... =	3·45*	4·05†	4·7	5·45‡	6·3‡	6·8‡	7·15‡

Bromphenol-blue.

x ..... =	4·6	4·7	4·8	4·9	5·0	5·1
p_{H} ..... =	3·35*†	3·55*†	3·75*†	3·9*†	4·4	4·85

Congo-red.

x ..... =	4·6	4·7	4·8	4·9	5·0
p_{H} ..... =	3·25*	3·35*	3·63*	3·8*	4·2

Litmus.

x	= 5·2	5·4	5·5	5·6
p_H	= 5·9‡	6·4‡	6·55‡	6·98‡

Phenol-red.

x	= 5·63	6·13	6·65	7·16	7·67
p_H	= 7·2‡	7·6‡	7·8‡	7·95‡	8·05‡

Thymol-blue.

x	= 8·18	8·69	9·2	9·71
% acid neut.	=80	85	90	95
p_H	= 8·1‡	8·3‡	8·55‡	8·95‡

FIG. 1.

The neutralisation of selenious acid.



⊙ *Experimental.* + *Calculated from present constants.* × *Calculated from Blanc's constants.*

The mean values of $10^3 \times K_1$ calculated from equations (*a*) and (1) above are: Thymol-blue, 4·18*; bromphenol-blue, 3·3*, 3·22†; congo-red, 4·32*; B.D.H. indicator, 4·37*†. Allowance being made for the number of observations, the general mean is: $K_1 = 4{\cdot}0 \times 10^{-3}$.

The mean values of $10^8 \times K_2$ are: B.D.H. indicator, 0·62;

litmus, 1·15; phenol-red, 0·72; thymol-blue, 1·04. The general mean is : $K_2 = 0{\cdot}87 \times 10^{-8}$.

A few values of p_H calculated from these constants are represented by + on the graph, *i.e.* :

% acid neut.	0	50	50·5	54·0	74·4	95·25	100
p_H ..... =	1·86	5·23	6	7	8	9	10·35

The experimental results are represented by circles, and the values calculated from Blanc's constants, at a molarity of 0·05, by ×.

% acid neut. =	0	0·7	12·5	35·5	41·5	47·7	50·05	50·4
p_H ..... =	1·99	2	2·3	3·0	3·3	4·0	5	5·3
% acid neut. =	52·4	54·6	66·5	75·25	91·5	95·5	99·05	
p_H ..... =	6·0	6·3	7·0	7·3	8·0	8·3	9·0	

The first branch of Blanc's curve lies distinctly above ours. The second branch of our curve has a very different position from Blanc's, the alkalinities throughout being greater.

The end-points in the titration of 0·05*N*-acid are :

	$NaHSeO_3$.	Na_2SeO_3.
Blanc	4·93	9·70
W. & P.	5·23	10·35

The choice of *p*-nitrophenol for the first titration is justified, and cochineal, lacmoid, and resazurin also should be suitable.

The second end-point does not of course give so accurate a titration, but we have obtained fair results with thymolphthalein (to a full blue). Tropæolin O is not so good.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, April 27th,* 1925.]

CCVI.—*The Interaction of Carbon Dioxide and Hydrogen on the Surface of Tungsten.*

By CYRIL NORMAN HINSHELWOOD and CHARLES ROSS PRICHARD.

ACCORDING to Taylor (*Proc. Roy. Soc.*, 1925, *A*, **108**, 105), only a small fraction of a catalytic surface is necessarily active and this fraction is a function, not merely of the surface itself, but also of the reaction catalysed. This theory, which is based upon evidence of different kinds, was very helpful in interpreting the results of our investigation of the interaction of carbon dioxide and hydrogen on the surface of platinum, and other experiments (this vol., p. 806), where complete lack of correlation was sometimes found between total adsorption and that part of the adsorption which determines the kinetics of heterogeneous reactions. These all lend support to Taylor's view that catalysis may be confined to certain active centres.

In continuation, the interaction of carbon dioxide and hydrogen on the surface of tungsten has been investigated. Kinetically, the reaction is somewhat different from the reaction on the surface of platinum, but there is equally good evidence that it is determined by the adsorption of carbon dioxide and hydrogen on active centres. From measurements of the velocity of reaction, it must be inferred that saturation of the active surface with respect to each of the gases is reached without any appreciable displacement of the other. Saturation may be reached simultaneously and independently with respect to each. This seems to show that those centres which adsorb the carbon dioxide are not the same as those which adsorb the hydrogen, and that interaction requires the adsorption of molecules of each on adjacent centres of the appropriate kind.

The experimental method was essentially the same as that used in the previous investigation except that the reaction vessel was now a tungsten filament Osram lamp (30 volt, half-watt) to which were sealed capillaries leading to gas-holders, manometer and Gaede pump. The temperature of the filament was calculated from its resistance with the aid of Langmuir's data for the variation of the resistance of tungsten with temperature (*Physical Rev.*, 1916, **7**, 159).

The reaction was rendered irreversible by the absorption of the water formed in concentrated sulphuric acid in the bottom of the reaction vessel.

It was shown by analysis that under the conditions of the experiments the only reaction taking place to an appreciable extent was the simple change $H_2 + CO_2 = H_2O + CO$.

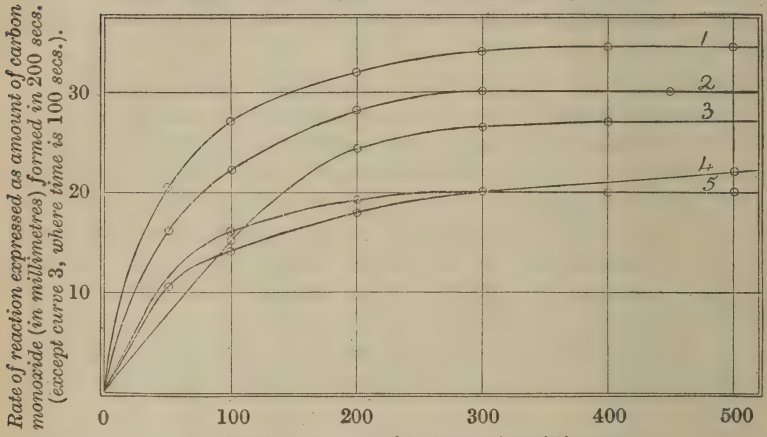
Pure carbon monoxide rapidly attacks a heated tungsten wire with formation of carbonyl, and the resistance of the wire increases very rapidly. Under the conditions of our experiments, however, the carbon monoxide produced in the reaction had no effect on the wire. Whether this was because the pressure was not great enough or because the other gases had a protecting action on the wire was not investigated, but it was ascertained with the greatest care that the resistance of the wire remained constant and, an even more delicate test, its catalytic activity remained remarkably steady. Control experiments under standard conditions were repeatedly made to ensure that the results were not being vitiated by any change in the wire.

Influence of the Pressure of the Hydrogen on the Rate of the Reaction.—Experiments were made with a constant pressure of carbon dioxide and varying hydrogen pressures. The rate of reaction first increases with the pressure of hydrogen and then remains constant, showing that the active part of the surface becomes saturated with hydrogen.

This is illustrated in Fig. 1. The curves were obtained with four different wires, the saturation capacities of which were naturally slightly different. The reaction–time curves are almost linear over a considerable range, so that the amount of carbon monoxide formed in 100 or 200 seconds is a quite legitimate and convenient measure of the initial rate of reaction. The following figures were obtained with one of the four wires used.

FIG. 1.

Relation between rate of reaction and hydrogen pressure.



(1) *Wire* 1, 50 *mm.* CO_2, 1182°; (2) *Wire* 3, 50 *mm.* CO_2, 1135°; (3) *Wire* 1, 100 *mm.* CO_2, 1182°; (4) *Wire* 5, 50 *mm.* CO_2, 1027°; (5) *Wire* 2, 50 *mm.* CO_2, 1215°.

TABLE I.

Influence of Hydrogen Pressure.

Pressure of carbon dioxide = 50 mm. in each case. Temperature = 1182°.

Press. of H_2 (mm.) $[H_2]$.	% CO_2 changed to CO in 100 sec.	200 sec.	300 sec.	Press. of H_2 (mm.) $[H_2]$.	% CO_2 changed to CO in 100 sec.	200 sec.	300 sec.
50	22	41	56	300	40	68	85
100	30	54	74	400	41	70	86
200	36	63	82	500	41	66	84

If σ is the fraction of the active surface covered with hydrogen, then the simplest type of adsorption equilibrium is expressed by $k_1(1 - \sigma)[H_2] = k_2\sigma$, whence $\sigma = [H_2]/(k_2/k_1 + [H_2])$.

Taking the readings at 100 seconds as proportional to initial velocities, a procedure justified by the almost linear form of the curves, and calling x the limiting rate at infinite hydrogen pressure,

we have for $[H_2] = 50$, $\sigma = 22/x$ and for $[H_2] = 100$, $\sigma = 30/x$; whence we find $x = 47$ and $\sigma = [H_2]/(57 + [H_2])$.

The following table gives the values of σ calculated from this equation, and also calculated on the supposition that the fraction of the active surface covered with hydrogen is given by the ratio of the actual velocity to the limiting velocity. This is referred to as $\sigma_{obs.}$

$[H_2]$	(50)	(100)	200	300
$\sigma_{obs.}$	(0·47)	(0·64)	0·77	0·85
$\sigma_{calc.}$	(0·47)	(0·64)	0·78	0·84

At 400 and 500 mm. $\sigma_{obs.}$ falls below the calculated value, that is to say, the rate of reaction does not increase quite as rapidly as it should. Indeed the calculated limiting rate is 47% of carbon dioxide transformed in 100 seconds, whilst the observed limiting rate is 41%. The hydrogen therefore has a certain displacing action on the carbon dioxide at higher pressures, but, as the table shows, this is negligible up to 300 mm. and even above this the displacing action is not wholesale as it would be if both gases competed for the same portions of the surface. Other wires gave similar results as the diagram shows, but detailed figures need not be given.

Influence of the Pressure of the Carbon Dioxide on the Rate of Reaction.—This is similar to that of the hydrogen pressure, but saturation is reached at lower pressures and a slight diminution in the rate of reaction occurs at the highest pressures. This indicates that the carbon dioxide can displace hydrogen to some slight extent, but the effect is almost negligible compared with that found when a platinum wire is used.

Table II.

Influence of Carbon Dioxide Pressure.

Pressure of hydrogen = 50 mm. in each case. Temperature = 1182°.

Press. of CO_2 (mm.)	% total possible CO formed in			Press. of CO_2 (mm.)	% total possible CO formed in		
$[CO_2]$.	100 sec.	200 sec.	300 sec.	$[CO_2]$.	100 sec.	200 sec.	300 sec.
50	22	40	54	300	25	45	60
100	24	46	62	400	22	39	52
150	24	45	60	450	20	35	48
200	24	45	60	500	18·5	33·5	46

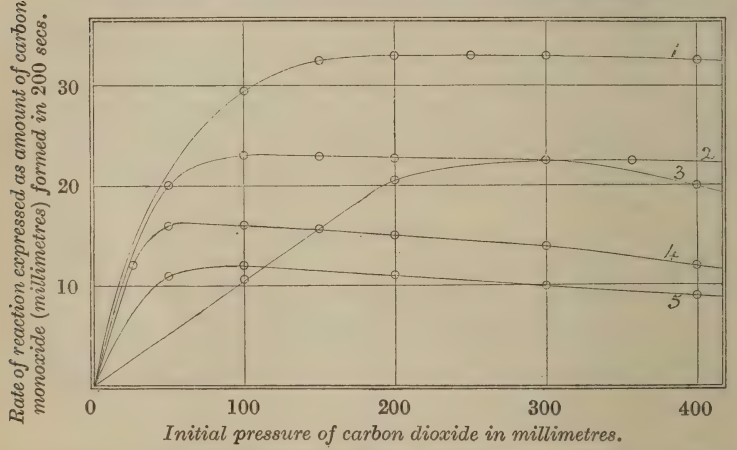
Taking the saturation value as 25 and ignoring the slight displacement effect at 400 and 500 mm., $\sigma_{CO_2} = [CO_2]/(5 + [CO_2])$ is found to represent the fraction of the active surface covered with carbon dioxide at various pressures.

Typical curves obtained with various wires are shown in Fig. 2.

The Kinetics of the Reaction.—We have seen that the surface can apparently become saturated with hydrogen and carbon dioxide independently. Thus, for example, the experiments in which the pressure of the carbon dioxide is varied show that the surface is nearly saturated with respect to this gas at 50 mm. pressure. Yet with 50 mm. of carbon dioxide the hydrogen pressure can be increased from 200 to 500 mm. with little change in the reaction rate. If hydrogen displaced carbon dioxide, the rate would pass through a pronounced maximum, as it does in the experiments where carbon dioxide displaces hydrogen from certain active points on platinum surfaces.

FIG. 2.

Relation between rate of reaction and carbon dioxide pressure.



(1) *Wire* 1, 100 *mm.* H_2, 1182°; (2) *Wire* 1, 50 *mm.* H_2, 1182°; (3) *Wire* 2, 100 *mm.* H_2, 1215°; (4) *Wire* 3, 50 *mm.* H_2, 1135°; (5) *Wire* 5, 50 *mm.* H_2, 1027°.

If we have nearly independent adsorptions in this way, the simplest assumption to make is that the rate of reaction is proportional to $\sigma_{H_2}\sigma_{CO_2}$.

From the results of the previous section we should therefore have

$$\text{Rate of reaction} = k \cdot \frac{[H_2]}{(57 + [H_2])} \cdot \frac{[CO_2]}{(5 + [CO_2])}.$$

The factors $[H_2]/(57 + [H_2])$ and $[CO_2]/(5 + [CO_2])$ were found from experiments with pressures of 50 mm. of carbon dioxide and hydrogen respectively. Using them, we may test the constancy of k at other pressures. The following are some typical experiments, all carried out at 1182°.

	Amount of carbon monoxide (mm.) formed in time t.			
t (seconds).	50 mm. H_2 \ 50 mm. CO_2 /	100 mm. H_2 \ 100 mm. CO_2 /	200 mm. H_2 \ 200 mm. CO_2 /	300 mm. H_2 \ 300 mm. CO_2 /
100	11·5	18·5	23	29
200	20	34	46	58
300	27	46	64	87
400	32	56	87	116
500	36·5	—	105	—
	$k = 27$	$k = 30$	$k = 30$	$k = 35$

The following table gives values of k for a number of similar experiments. In every case the rate of reaction from which k is obtained is expressed as the amount of carbon monoxide produced in 100 seconds. All the figures refer to wire 1.

Press. of CO_2 (mm.).	Press. of H_2 (mm.).	k.	Press. of CO_2 (mm.).	Press. of H_2 (mm.).	k.
50	100	26	100	50	25·5
100	100	25	100	100	25
150	100	27·5	100	150	27
200	100	27·5	100	200	31·5
300	100	27	100	300	31
500	100	27			

The idea of independent adsorption of the two reacting substances thus seems to be substantiated.

The Influence of Temperature.—The temperature coefficient of the reaction rate was measured with one only of the wires. Experiments were made with a standard mixture of hydrogen (100 mm.) and carbon dioxide (100 mm.) at each temperature.

CO (pressure in mm.) formed in	Temperature.				
	953°.	1061°.	1135°.	1231°.	1303°.
100 secs.	2	5·5	11	21	29
200 „	4	11	22	38	51
300 „	7	16	33	52	—

The value of the apparent heat of activation calculated from these by means of the Arrhenius formula is 30,000 calories.

Summary.

The rate of the reaction $H_2 + CO_2 = H_2O + CO$ on the surface of a tungsten filament heated to temperatures between 1000° and 1300° is proportional to $\sigma_{H_2} \cdot \sigma_{CO_2}$, where σ_{H_2} and σ_{CO_2} are the fractions of certain active parts of the surface which are covered with adsorbed hydrogen and carbon dioxide respectively.

The adsorption of each gas on the active centres is almost independent of the pressure of the other. This shows that the whole surface is not active, but that only certain parts are able to adsorb hydrogen and carbon dioxide and cause them to react. The parts which adsorb hydrogen in this way are different from those which

adsorb and render reactive the carbon dioxide. Interaction apparently takes place when molecules of the two gases are adsorbed on adjacent centres of the appropriate kind.

We are indebted to the Royal Society and to the Chemical Society for grants with which some of the apparatus used was purchased.

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[*Received, June 3rd*, 1925.]

CCVII.—*The Relation of Homogeneous to Catalysed Reactions. The Catalytic Decomposition of Hydrogen Iodide on the Surface of Gold.*

By CYRIL NORMAN HINSHELWOOD and CHARLES ROSS PRICHARD.

A HETEROGENEOUS catalyst may influence a reaction in two ways. It may modify the mechanism of the chemical change by allowing it to proceed along another path. It may also facilitate the transformation by lowering the energy of activation, *i.e.* the energy which must be imparted to the reacting molecules before they can be transformed chemically. There is very good evidence that in homogeneous chemical changes this energy of activation is the quantity which plays the decisive part in determining the rate at which the reaction can take place at a given temperature. It must therefore be expected to have considerable significance in catalytic reactions also.

The modification of reaction mechanisms is exemplified by the thermal decomposition of nitrous oxide. The homogeneous reaction is bimolecular (*Proc. Roy. Soc.*, 1924, *A*, **106**, 284). On the surface of platinum or gold the change becomes unimolecular (*Proc. Roy. Soc.*, 1925, *A*, **108**, 211; this vol., p. 327). It is resolved into the stages $N_2O = N_2 + O$ and $O + O = O_2$. The affinity of the metals for atomic oxygen renders possible the first stage, which could only take place homogeneously if a very large amount of energy were communicated to the nitrous oxide molecule, for the production of free oxygen atoms is a highly endothermic process. The metal acts as a resting place for the oxygen atoms until they meet others of their kind. It appears also that on the surface of platinum ammonia decomposes unimolecularly (this vol., p. 1105), whilst, although the homogeneous reaction has not been actually observed, it is almost certain from analogy with known examples that it would be bimolecular.

The question of the influence of the second factor, the lowering of the energy of activation, has not received a conclusive answer. The nitrous oxide decomposition is the only example hitherto investigated in which a homogeneous reaction has been quantitatively compared with the corresponding heterogeneous change on one or more surfaces. The homogeneous transformation requires the collision of two molecules possessing a combined energy of 58,500 calories. This quantity can be obtained from the temperature coefficient of the reaction velocity. The corresponding heats of activation obtained in the same way from the temperature coefficients of the surface reactions on gold and platinum are 29,000 and 32,500 calories, respectively. But it is not quite justifiable to compare these various values directly. In the case of bimolecular homogeneous reactions, there is ample evidence that the heat of activation is a real measure of the energy that the colliding molecules must possess in order that they may be transformed (compare J., 1924, **125**, 1841). In heterogeneous reactions, however, the temperature coefficient of the reaction velocity depends partly on the variation with temperature of the amount of reactant actually adsorbed on the surface, and therefore the value of E obtained from the formula $d \log k/dT = E/RT^2$ requires correction before it represents the energy which the adsorbed molecules must acquire in order to undergo chemical change (compare J., 1923, **123**, 1014). There exists a real temperature coefficient of the rate of reaction of the molecules actually adsorbed. This would furnish a true value for the heat of activation having direct physical meaning, but since the relative numbers of molecules of reactant adsorbed at different temperatures are not known, the correction which would make the observed reaction velocities at various temperatures directly comparable with one another cannot be applied. The adsorption of the reacting gas diminishes with temperature. This acts in opposition to the normal increase of the true reaction rate with temperature and thus the observed temperature coefficient is less than the true value. Thus $E_{obs.}$ is too small. It is likely that the necessary correction is quite small compared with 30,000 calories, so that we are probably safe in concluding that the total activation required in each of the surface reactions of the nitrous oxide is much less than in the homogeneous reaction. It is true that the 58,500 calories refers to 2 gram-molecules, whilst the values 29,000 and 32,500 refer to 1 molecule only, the catalytic reactions being unimolecular. But the fact remains that the total activation necessary in the surface reaction is very much less, since in the homogeneous reaction one molecule is not activated without the other.

These conclusions are interesting, but not free from a little uncertainty, arising from the lack of knowledge about the exact correction that should be applied to the experimentally found heats of activation in the surface reactions. The object of this paper is to present results which are free from any such uncertainty.

The difficulty to be overcome is the unknown variation in the degree of adsorption of the reacting substance at different temperatures. The difficulty vanishes in one special case, namely, when the surface is saturated at all temperatures so that the number of molecules present is always the same. This state of affairs is recognised by the fact that the absolute rate of reaction becomes independent of the pressure of the reacting gas, or, in other words, the reaction is of zero order.

The heterogeneous decomposition of ammonia on the surface of tungsten was recently found to be approximately of zero order (this vol., p. 1105) and results are described in the present paper to show that the decomposition of hydrogen iodide on the surface of gold is also of this type. The observed heats of activation in these reactions are therefore equal to the true values and may be compared directly with the values for the corresponding homogeneous reactions.

The value found for the decomposition of hydrogen iodide on the surface of gold is 25,000 calories. Since the reaction is of zero order, it is impossible to tell whether one or two molecules of hydrogen iodide are involved in it; to decide this point is only possible with sparsely covered surfaces—when the surface is saturated, it makes no difference to the actual kinetics of the reaction whether one molecule decomposes spontaneously or two adjacent ones interact. From analogy with the case of nitrous oxide, it seems probable that only one is involved. However this may be, the total heat of activation is again very much lower than that of the homogeneous reaction, which amounts to 44,000 calories.

With regard to ammonia the homogeneous reaction has not been observed, but its velocity has been shown to be negligible up to 1050° (this vol., p. 1105). From analogy with the decompositions of ozone, chlorine monoxide, hydrogen iodide, and nitrous oxide, it seems certain that it would be found to be bimolecular, and from the table given by Hinshelwood and Hughes (J., 1924, **125**, 1841), showing the relation between the heat of activation of bimolecular reactions and the temperatures at which they attain a given rate, it is obvious that the heat of activation in the homogeneous ammonia decomposition cannot be less than about 80,000 calories. The heat of activation of the reaction on the surface of tungsten was found to be 38,700 calories.

The following table gives a summary of the various relationships :

Reaction. Thermal decomposition of	Total activation required for the homogeneous change (bimolecular).	Total activation required for the heterogeneous change (probably or certainly unimolecular).
Hydrogen iodide	44,000	25,000 (gold)
Nitrous oxide	58,500	29,000 * (gold)
		32,500 * (platinum)
Ammonia	probably >80,000	39,000 (tungsten)

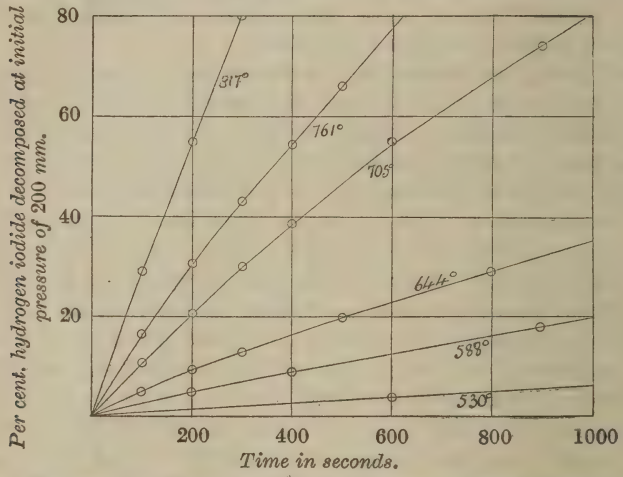
* + small correction ?

(The decomposition of ammonia on platinum cannot be brought into this table because it is retarded by the hydrogen formed in such a manner as to make the temperature coefficient mainly a function of the hydrogen adsorption.)

It will be observed that the values for the surface reactions are in each case approximately half the corresponding values for the homogeneous reactions. There is perhaps some temptation to suppose that the numerical ratio of 2 : 1 would be exact if perfectly accurate data could be obtained, and to interpret this in terms of activation by one and two quanta. This, however, is not admissible. Activation doubtless takes place in accordance with quantum dynamics, but the characteristic quanta involved in reactions taking place under physical conditions so different as to lead to completely different reaction rates cannot be expected to bear any simple numerical relation to one another. When the stability of a molecule is profoundly modified, it can only be as the result of a rearrangement of the internal forces which will also lead to a fundamental change in the size of the quanta. We must at present content ourselves with observing the greatly decreased heat of activation in the surface reactions and the probable change from bimolecular to unimolecular processes.

The Catalytic Decomposition of Hydrogen Iodide on Gold.—The experimental procedure for measuring the rate of decomposition of hydrogen iodide on the surface of a heated gold wire was exactly as described in previous papers (this vol., p. 327; *Proc. Roy. Soc.*, 1925, *A*, **108**, 211). The iodine liberated in the reaction was condensed on the walls of the vessel, which was kept at 0°. The vapour pressure of iodine at 0° is negligible. The reaction $2HI = H_2 + I_2$ is therefore accompanied by a decrease in pressure which allows its rate to be measured. There existed the possibility that the gold wire might be attacked by the iodine. Gold iodide is, however, decomposed at 200°, and the lowest temperature of the wire in the experiments was 530°. Iodine, therefore, under the experimental conditions never had the opportunity of reaching

the wire except at a temperature several hundred degrees above that at which gold iodide ceases to be capable of existence. It should be mentioned that gold iodide is apparently endothermic, although F. Meyer finds that the interaction of gold and iodine diminishes with temperature and almost ceases above 190°. This leaves it just possible that there might be slight interaction again at higher temperatures. But it is in the highest degree unlikely that the dissociation pressure of gold iodide would at 800° have fallen below the minute iodine pressure prevailing in these experiments, and the special experiments made to test for interaction showed that it was in fact inappreciable. The change in pressure observed when the decomposition was complete coincided with the



Catalytic decomposition of hydrogen iodide with surface of gold. Initial pressure 200 mm.

theoretical value. The resistance of the wire at 0° was measured from time to time and found not to vary as it would if the gold were being attacked, and the catalytic activity remained constant. The action of the gold may therefore be regarded as purely catalytic in the usual sense of the term.

The hydrogen iodide was prepared by dropping syrupy phosphoric acid on a mixture of finely divided potassium iodide and phosphorus pentoxide in an apparatus made entirely of glass. The gas was dried by passage over phosphorus pentoxide and condensed in a bulb surrounded by liquid air. While the hydrogen iodide was kept solid, any non-condensible impurities such as hydrogen were pumped away. About one-third of the liquid was then allowed to distil into an evacuated blackened glass bulb, provided with a tap. This bulb was then sealed to the decomposition apparatus.

Since hydrogen iodide attacks mercury, special precautions have to be taken in measuring the reaction velocity with the aid of a mercury manometer. Fortunately, it was found that hydrogen has no influence on the velocity of decomposition and it was therefore convenient to allow the reaction always to proceed in the presence of a certain amount of hydrogen, which was let into the apparatus first and thus acted as a buffer in the capillary manometer, protecting the mercury completely from any attack by the hydrogen iodide.

The following figures show that hydrogen has no effect on the reaction velocity.

Temp. 705°. HI alone (200 mm.). Amt. decomposed in 200 secs. = 32 mm. HI (200 mm.), H_2 (100 mm.). Amt. decomposed in 200 secs. = 34 mm.

Temperature 705°.	Amount of hydrogen iodide decomposed (mm.).		
Time (sec.).	50 mm. H_2 \ 100 mm. HI /	100 mm. H_2 \ 100 mm. HI /	200 mm. H_2 \ 100 mm. HI /
100	19	18	18
200	35	36	34
300	49	50	47
400	61	62	59
500	72	72	68

The absolute amount of hydrogen iodide decomposed in unit time is nearly independent of its pressure. This may be seen by an inspection of the following results. It will also be observed that the curves shown in the figure are not far from linear.

Temperature 705°. 100 Mm. of hydrogen present in each expt.

Time (sec.).	Amount of hydrogen iodide decomposed. 100 mm. HI.		200 mm. HI.	400 mm. HI.	Time (sec.).	Amount of hydrogen iodide decomposed. 100 mm. HI.		200 mm. HI.	400 mm. HI.
100	18	18	22	26	800	88	90	—	—
200	34	36	42	46	900	—	—	148	174
300	48	50	60	—	1200	—	—	—	224
400	60	62	76	76	1500	—	—	—	266
500	69	72	—	—	1800	—	—	—	308
600	77	79	110	118	2100	—	—	—	334
700	—	—	—	—	2400	—	—	—	352

Temperature 588°.

Time (secs.).	Amount of hydrogen iodide decomposed. 200 mm. HI.	400 mm. HI.
200	10	11
400	18	—
500	—	26
900	36	44
1600	54	—

Temperature 817°.

Time (secs.).	Amount of hydrogen iodide decomposed. 100 mm. HI.	200 mm. HI.	400 mm. HI.
100	58	58	76
200	84	111	144
300	92	162	196
400	—	—	252
500	—	—	298
600	—	—	334
700	—	—	354

The reaction is thus nearly of zero order, a fourfold increase in pressure increasing the absolute reaction rate only in the ratio 1 : 1·45 at 705° and 1 : 1·46 at 817° instead of in the ratio 1 : 4·0, as would happen if the change were according to the unimolecular law.

The nearness of this ratio to unity shows that saturation of the surface is nearly reached at both temperatures and the equality of the ratio at the two temperatures shows that the deviation from saturation at a given pressure cannot differ appreciably in the two cases. The temperature coefficient should therefore be independent of the variation of adsorption with temperature.

The influence of temperature on the velocity of reaction was measured from 530° to 817°. From the slope of the line obtained by plotting the reciprocal of the absolute temperature against log t, where t is the time taken for 50 mm. out of an initial 200 mm. of hydrogen iodide to decompose, a value of 25,000 calories is found for the heat of activation. The same value is found from the times required for 20 mm. out of the initial 200 mm. to react.

Absolute temperature.....	803°	861°	917°	978°	1034°	1090°
t (seconds)	6000	1450	650	242	157	85

A discussion of these results has been given in the earlier part of the paper.

Summary and General Conclusions.

It is shown that the thermal decomposition of hydrogen iodide on the surface of a heated gold wire is a catalytic reaction the rate of which is almost independent of the pressure of the gas and uninfluenced by the presence of hydrogen.

It is pointed out that such " zero-order " reactions are of special importance because their temperature coefficients are not influenced by the changing degree of adsorption of the reactant. The " heat of activation " may therefore be expected to have, without correction, the direct physical significance that it possesses in the case of homogeneous reactions.

On the basis of the results described in this and previous papers it is now possible to make a comparison between the mechanism of homogeneous reactions and that of the corresponding reactions catalysed by surfaces.

The reactions considered are the homogeneous thermal decomposition of nitrous oxide, hydrogen iodide, and ammonia, and the heterogeneous decomposition of nitrous oxide on platinum and gold, of hydrogen iodide on gold, and of ammonia on tungsten.

It is shown that the surface reactions have heats of activation only about half as great as those of the bimolecular homogeneous changes. But the surface reactions have been shown in some cases

to involve only one molecule, and this is probably the general rule. Thus the function of the surfaces in the reactions considered is to permit the occurrence of a unimolecular process instead of a bimolecular process requiring an energy of activation about twice as great.

We are indebted to the Royal Society and to the Chemical Society for grants in aid of this work.

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CCVIII.—*The Adsorption of Water from the Gas Phase on Plane Surfaces of Glass and Platinum.*

By IVAN ROY MCHAFFIE and SAM LENHER.

THE results of numerous investigators (Ihmori, *Ann. Phys. Chem.*, 1887, **31**, 1006; Briggs, *J. Physical Chem.*, 1905, **9**, 617; Trouton, *Proc. Roy. Soc.*, 1907, *A*, **79**, 383; Katz, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 445; Parks, *Phil. Mag.*, 1903, **6**, 517) would indicate that the film of water adsorbed on a glass surface at the ordinary temperature from the gas phase may be of more than monomolecular thickness when the pressure of water vapour is not far removed from the saturation value at the corresponding temperature. Langmuir (*Proc. Faraday Soc.*, 1922, 607; *Physical Rev.*, 1915, **6**, 79), in stating his important theory of adsorption, says, "Only when we have saturated vapours should we ever get films of gas molecules of more than monomolecular thickness." The present research is a study of the films of water adsorbed from the gas phase on plane glass and platinum surfaces when the pressure of the water vapour is near the saturation value.

The method employed is such that a direct measurement of the number of molecules adsorbed from a saturated vapour on a known area of a plane surface can be made. The phenomenon on which this study of adsorption is based was observed by one of us in another research and may be briefly stated as follows. Consider a closed, evacuated system into which a limited mass of water is introduced. This mass must be such that at some higher temperature the entire amount will be in the state of vapour, but at the initial temperature part of the water exists in the liquid phase, the remainder being in the gas phase. The pressure in the system due to water vapour should be equal to the vapour pressure of water at the initial tem-

perature, and the pressure at successively increasing temperatures should be equal to the vapour pressure of water at the corresponding temperatures until all of the water present has passed into the gaseous phase.

The increases of pressure above this value due to increasing temperatures should be proportional to the absolute temperature. If the temperatures be plotted as abscissæ and the corresponding pressures as ordinates, the curve obtained from these theoretical considerations would be *aob* (Fig. 2). The portion *ao* is the vapour-pressure curve for water and *ob* is the curve showing the effect of temperature on the pressure of a gas at constant volume. The values of pressure in the system as a function of temperature, determined experimentally, do not agree with these theoretical considerations. The experimental curve for such a system is *acb* (Fig. 2). At temperatures below the point *a* the experimental curve coincides with the vapour-pressure curve for water (*ao*), and at the temperatures above the point *b* the experimental curve coincides with the theoretical curve *ob*. The measurements of pressure at temperatures between *a* and *b* are in every case less than those expected from the simple theory given above. The greatest deviation of the experimental curve from the theoretical curve is at the temperature given graphically by the point *o*. At this temperature all the water in the system should be in the gaseous phase, if adsorption did not occur, and the pressure due to water vapour should be equal to the vapour pressure of water at this temperature. If the temperature and the pressure of the system are those of the point *b*, then all of the water present exists in the gaseous phase. The pressures determined experimentally at successively decreasing temperatures between *b* and *o* should be those represented by the line *bo*, if adsorption did not occur, but the values of pressure determined lie along the curve *bc*; continued pressure measurements at temperatures between *c* and *a* give the curve *ca*, the experimental curve from *a* to *b* being a smooth continuous curve.

The pressure measured at any temperature between *a* and *b* is less than the expected value. This decrease of pressure must be due to adsorption of water from the gas phase. That equilibrium is established along the curve is evident from the fact that at any one temperature the value of the pressure measured is the same whether the system be heated to that temperature or cooled down from a higher one.

It is not possible to state definitely from the findings of this research whether the adsorption measured takes place directly on the solid surface of the glass or platinum, or on the surface of a stable adsorbed layer of water which is on the surface throughout

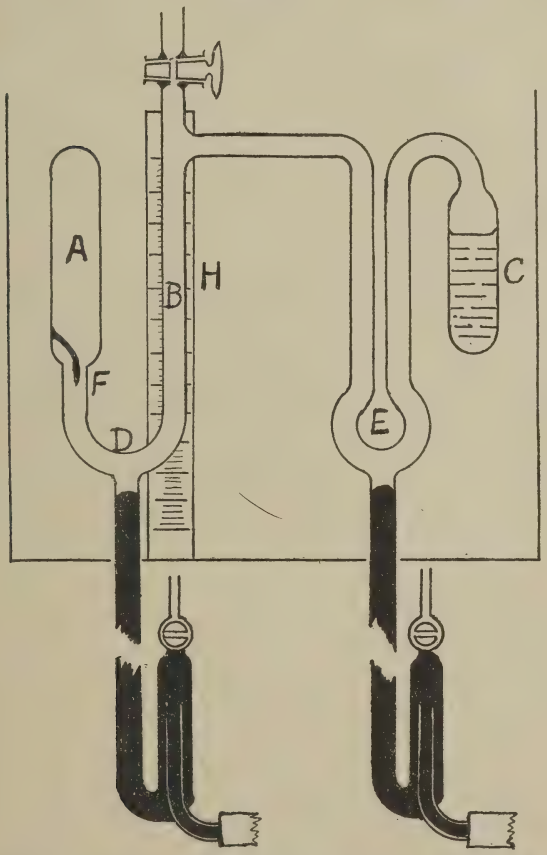
all of the experiments. The procedure adopted is such that this question cannot be settled here.*

The method of experimentation was as follows.

The Adsorption of Water on a Glass Surface.

The Apparatus.—A diagram of the apparatus employed to measure the pressures in a constant-volume system is shown in Fig. 1.

FIG. 1.



A is a hollow cylindrical tube of soft Duroglass closed at the top end; the lower end is sealed to a glass tube of smaller diameter

* The adsorbing surfaces in the case of glass or platinum (the materials employed in this investigation) are not of course ideally plane as assumed in this paper, and so the amount of substance adsorbed per unit of area of adsorbing surface may be smaller than as calculated. A discussion of this question is reserved for a subsequent paper.

which is bent into a U, D. At the bottom of the U a glass tube 78 cm. long is sealed; a mercury air-trap is sealed to the bottom end of this tube, which is in turn attached to a mercury reservoir by means of rubber tubing. The internal dimensions of A were carefully measured before the tube was constructed; tubing of uniform bore and as free as possible from imperfections was chosen. The tube was annealed for 4 hours at 500°. The internal surface of the tube A was cleaned by first washing with organic solvents. The tube was then filled with freshly prepared chromic acid cleaning solution and allowed to stand for 24 hours. The cleaning was completed with fuming nitric acid and repeated washings with distilled water. The volume of the tube to the pointer F was calibrated to 0·005 c.c. The open end of the U, D, is connected to mercury diffusion pumps and a McLeod gauge. A tap is placed in the tube B. A few cm. below the tap a side tube is sealed making connexion with a second U tube, E, the other end of the U is sealed to a bulb, C, containing distilled water.

To the bottom of the U, E, a tube similar to that at the bottom end of D is sealed and is connected as before to a mercury reservoir. In making the final position seals in the clean apparatus the glass blowing was done through a phosphorus pentoxide tube. All the mercury used in the apparatus was thoroughly purified and dried by the usual methods. The whole was mounted vertically in a water thermostat, the temperature of which was maintained and controlled electrically, the thermoregulator permitting of an adjustment over a long range of temperature. The tubes from D and E passed through stuffing boxes in the bottom of the thermostat. A scale, H, calibrated to 0·01 mm., was mounted behind the tube B. Plate glass windows were set in the sides of the thermostat so that the differences in level between the mercury in F and B might be read by means of a cathetometer provided with a micrometer screw adjustment. Evacuation was carried out by means of a diffusion pump backed by a Töpler pump. Pressure readings at high vacuum were made by the McLeod gauge. Before the apparatus was used for any determinations the air was entirely removed from the apparatus and from the water in C.

Experimental Procedure.—The mercury in D and E is lowered and the pressure of the air reduced by means of the water pump to such a value that the water in C just begins to boil. Excessive boiling must be avoided, otherwise water will be carried over from C into the U, E. The mercury is then raised in E, and the evacuation continued by the diffusion pump until the pressure remaining in the apparatus cannot be read on the McLeod gauge. The tap B is then closed and the mercury lowered in E.

When sufficient time has elapsed for the pressure to come to equilibrium with the vapour pressure of the water in C, the mercury in E is again raised and evacuation continued. This process is carried out a sufficient number of times so that the last remaining traces of air in C are removed. The position of the pointer F is now determined relative to the scale H.

When the vacuum is as high as possible, the mercury in D is raised until the tip of the pointer just touches its reflected image in the mercury meniscus. The position of the meniscus in B is then read off to 0·01 mm. on the scale H. This determination of the "zero" position of the pointer was carried out a number of times and in every case concordant results were obtained. The tap B is then closed and the mercury lowered in D and E. The temperature of the thermostat is adjusted so that the value of the pressure in A due to water vapour, and hence the mass of water in A, is that desired for a particular measurement. During the filling process the mercury in D and E is lowered just below the bottom of the U's so that any condensation of water on the mercury surfaces is avoided. The mercury is then raised in D and E, B is opened, and the apparatus completely evacuated to the mercury surfaces. The pressure in A is then determined by raising the mercury in D until the tip of the pointer just touches its reflected image, and reading off with the cathetometer the position of the meniscus in B on the scale H. The difference between this value and that of the "zero" position of the pointer is the pressure in mm. of mercury at the temperature of the thermostat exerted by the water vapour in A. From this reading it is possible to decide whether or not the desired amount of water has been admitted to A. If it is not sufficient, the temperature of the thermostat is increased, and the filling operation again performed. If too much water has been admitted, B is closed, the mercury is lowered in D, permitting some of the water vapour to escape into B, the mercury is then raised in D, the tap B is opened, and the portion of the apparatus above the mercury surfaces is further evacuated. This procedure is continued until the amount of water in A is that desired. It is not essential at this stage to know exactly the mass of water which has been admitted to A, since the mass may be determined from later measurements. Readings of the pressure in A are made both at successively increasing and decreasing temperatures, and in both instances readings obtained at any one temperature agree to 0·01 mm. The temperature is increased until the water vapour is behaving as a gas whose pressure at constant volume is increasing linearly with increasing temperature. The readings are continued at successively lower temperatures until the pressures measured agree as nearly

as possible with the vapour pressures of water at the corresponding temperatures.

Results.—The readings obtained in a series of measurements are given in Table I. T is the absolute temperature, and p the pressure read at the corresponding temperature in mm. of mercury at 0·0° C. The volume of the tube A was 13·307 c.c. and the area of the internal surface was 55·10 sq. cm.

TABLE I.

$T°$ abs.	p mm.	N/cm.^{2} $\times 10^{-14}$.	θ.	$-\Delta F$.	$T°$ abs.	p mm.	N/cm.^{2} $\times 10^{-14}$.	θ.	$-\Delta F$
		No. 1.					No. 2.		
293·0	16·90	1052·0	88·5	20·6	289·0	13·25	1387·0	117·0	—
298·0	22·73	616·4	51·8	26·1	293·0	16·92	1109·0	93·2	20·4
302·0	27·54	267·2	22·5	52·2	296·0	20·46	841·3	78·0	22·5
305·0	29·71	119·5	10·5	110·4	298·0	22·80	652·7	56·1	24·3
308·0	30·65	70·3	5·9	194·8	300·0	25·27	487·7	41·0	33·6
311·0	31·44	32·8	2·7	282·2	303·0	28·96	231·3	20·0	60·7
314·0	31·97	16·4	1·4	374·1	306·0	30·82	98·4	8·3	152·0
317·0	32·40	7·03	0·6	468·2	308·0	31·47	65·6	5·5	178·6
320·0	32·80	—	—	—	311·0	32·26	30·5	2·5	260·2
323·0	33·23	—	—	—	314·0	32·91	4·7	0·4	356·1
					317·0	33·31	—	—	—
					320·0	33·83	—	—	—
					323·0	34·19	—	—	—
		No. 3.					No. 4.		
293·0	16·99	1444·0	121·0	14·3	298·0	23·76	2188·0	184·0	0·0
298·0	23·08	986·6	83·0	17·1	301·0	27·85	1638·0	137·7	10·7
301·0	26·90	707·8	59·5	19·5	304·0	32·96	1265·0	106·0	13·3
304·0	31·06	407·7	34·0	49·1	307·0	37·85	918·8	77·2	32·2
307·0	34·26	185·1	15·5	92·7	310·0	43·07	550·8	46·3	54·5
310·0	35·92	86·7	7·2	165·7	313·0	47·02	286·0	24·0	98·6
313·0	37·05	25·8	2·1	248·5	316·0	48·70	194·5	16·3	179·1
316·0	37·79	—	—	—	319·0	51·55	21·1	1·4	237·4
					322·0	52·32	—	—	—
					325·0	53·11	—	—	—
					328·0	53·75	—	—	—

In Fig. 2 the values of T given in Table I are plotted as abscissæ and the corresponding values of p as ordinates. The vapour-pressure curve for water is also given, plotted from the data of Scheel and Heuse (*Ann. Phys.*, 1910, **31**, 715).

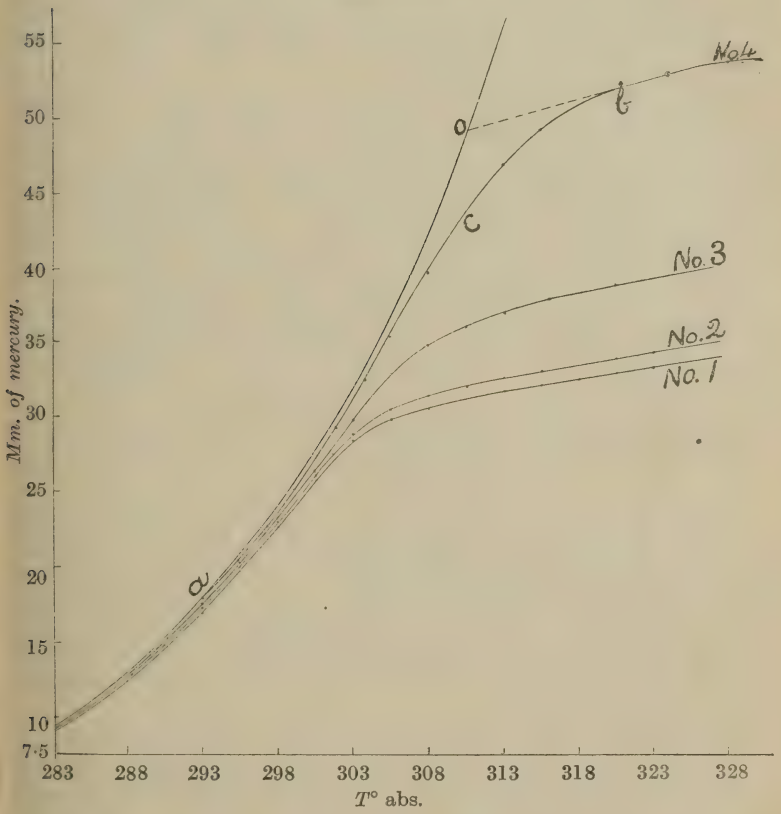
At the higher temperatures the values of p are increasing linearly with increasing temperature. The mean value of the rate of increase per degree is 0·0037. This is sufficiently near the temperature coefficient of a perfect gas that water vapour at these concentrations may be considered to behave as such. Hence the mass of water present in the system may be calculated from the equation $pv = nRT$, where p is the pressure at some point on the linear portion of the experimental curve at the temperature $T°$; v is the volume of the system; n is the number of moles present; and R is the gas constant, which, if p is measured in mm., is equal to 6·244 $\times$

10^4 c.c.-mm. per degree. If any other point be chosen on the experimental curve, then the temperature and pressure will be T_1 and p_1. The number of moles of water in the gaseous phase can be calculated at the new temperature and pressure and is given by $n_1 = p_1 v/RT_1$.

The number of moles adsorbed on the glass surface will be $n - n_1$, where $n - n_1 = pv/RT - p_1 v/RT_1$.

FIG. 2.

Glass–water.



The Avogadro number is $6{\cdot}06 \times 10^{23}$. The actual number of molecules adsorbed on the glass surface is $(n - n_1) \times 6{\cdot}06 \times 10^{23}$, or, if this number be denoted by N, then

$$N = \frac{v}{R}\left(\frac{p}{T} - \frac{p_1}{T_1}\right) \times 6{\cdot}06 \times 10^{23}.$$

Since v, the volume of the apparatus, and R are constant,

$$N = (p/T - p_1/T_1) \times 1{\cdot}292 \times 10^{20}.$$

The area of the inside surface of the glass tube can be calculated to 0·05 sq. cm. In this calculation, the area of the glass pointer must be included. The value obtained was 55·10 sq. cm. The number of molecules adsorbed per sq. cm. (N/cm.^{2}) is given by,

$$N/\text{cm.}^2 = (p/T - p_1/T_1) \times 2{\cdot}344 \times 10^{18}.$$

The degree of accuracy of this calculation is fairly high. The temperature was read to 0·05°; the pressure to 0·01 mm.; the volume was calibrated to 0·005 c.c., and the area calculated to 0·05 sq. cm. If the equation giving N/cm.^{2} be differentiated and these values be substituted for the corresponding differentials, the probable error in the calculation is 0·50%.

If the diameter of the water molecule be taken as $2{\cdot}9 \times 10^{-8}$ cm. (compare Jeans, "Dynamical Theory of Gases"), the number of molecular layers in the adsorbed layer may be calculated. The only assumption made, other than that made in the determination of the diameter, is that each molecule in a monomolecular layer occupies a square area each side of which is equal in length to the molecular diameter. No assumption is necessary concerning the packing of one layer on another. The surface of the glass may be considered as a plane surface. The number of molecules in a single layer covering an area of 1 sq. cm. is $1/d^2$, where d is the diameter of the molecule.

The number of layers in an adsorbed film will be $N/\text{cm.}^2 \div 1/d^2$. If this value be denoted by θ, then

$$\theta = (p/T - p_1/T_1) \times 1972.$$

Table I, column 3, gives the total number of molecules adsorbed per sq. cm. (N/cm.^{2}) at the temperatures $T°$ for each curve in Fig. 2; Table I, column 4, gives the thickness, θ, of the film in molecular layers. In Table I, No. 4, the initial reading at 298° abs. is that of a film the equilibrium pressure of which is equal to that of water in bulk. Such a film is produced when 2188×10^{14} molecules are adsorbed per sq. cm.

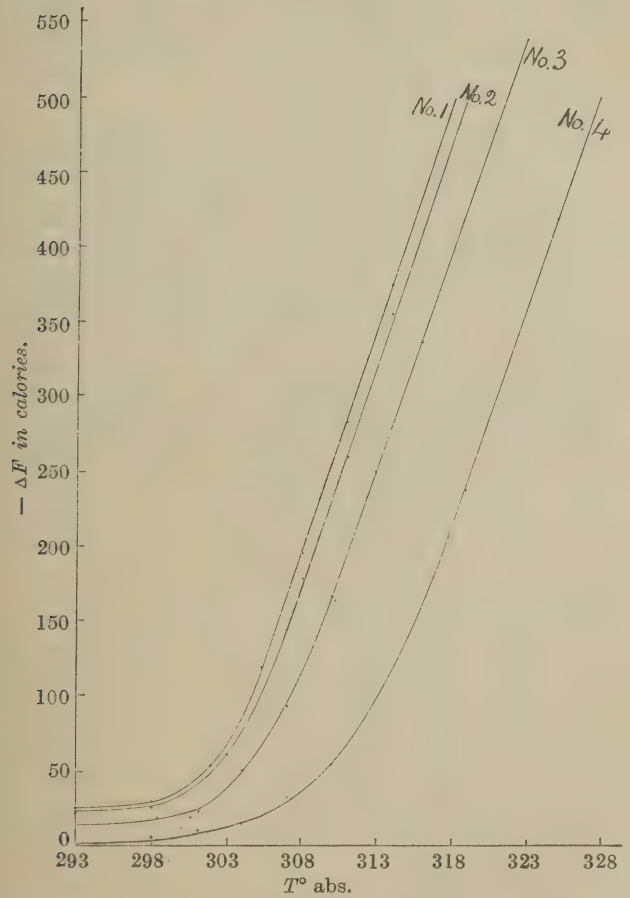
The experimentally measured pressure on any curve in Fig. 2 at any temperature is the equilibrium pressure between the film of water adsorbed on the glass surface and the water in the gaseous phase in the system. Taking as a standard state that of saturated water vapour at each temperature, it is possible to calculate from the experimental data the decrease of free energy, $-\Delta F$, corresponding to the adsorbed film. These values of $-\Delta F$ are calculated from the well-known thermodynamic equation, $-\Delta F = RT \log (p/p_1)$, where p is the vapour pressure of water at $T°$, p_1 is the equilibrium pressure of the adsorbed film at the same temperature, and R is the gas constant in calories per degree. The values of

$-\Delta F$ in calories per mol. of water adsorbed are given, together with the corresponding temperatures and thicknesses of film, in Table I.

The changes of free energy are shown graphically as a function of temperature in Fig. 3. It is evident from these curves that the

FIG. 3.

Glass–water.



free energy change accompanying the adsorption of water on glass is increasingly less for each new layer adsorbed.

Further discussion of these results will be more fruitful after the results for the adsorption of water on platinum have been given.

The Adsorption of Water on a Platinum Surface.

By a modification of the apparatus, as shown in Fig. 1, the adsorption of water from the gas phase on the surface of platinum was studied. The tube A, Fig. 1, is cut from the apparatus and a platinum tube, constructed to given internal dimensions, is sealed in its place. The volume is accurately determined before the tube is mounted in the apparatus. The inner surface of the platinum was polished, and thoroughly cleaned with concentrated nitric acid. The cleaning was completed by repeated washing with distilled water. The pointer F cannot be used in this experiment as the zero position at constant volume.

By the following method constant volume and constant adsorption surface of platinum were maintained. One terminal of an accumulator is connected to a voltmeter which is in turn in electrical connexion with the platinum tube, the other terminal of the accumulator is in electrical connexion with the mercury in the reservoir attached to D. When the mercury is lowered in D, the voltmeter does not register, but as soon as the mercury is raised until it touches the bottom end of the platinum tube the electrical circuit is completed and the voltmeter registers. By careful adjustment it is possible by this means to maintain a constant volume within the system.

The method of admitting water vapour to the system is identical with that already described. During each increase of temperature in a series of measurements, the mercury in F is raised a short distance into the platinum tube so that the water vapour does not adsorb on the glass surface of the tube F. When equilibrium has been established at the higher temperature, the mercury is carefully adjusted to the zero position and the pressure read as before. The methods of measuring the amounts of water adsorbed from the gas phase, and the calculations from the pressures measured, are in every case similar to those already described and need not be set out in detail here. The equation giving the free energy change is that already employed. The dimensions of the platinum tube are different from those of the glass tube, the volume being 5·317 c.c. and the area of the internal surface 15·36 sq. cm. The introduction of these values into the other equations alters the value of the constants as given below.

The measurements of pressure and the values of $N/\text{cm.}^2$, θ, and $-\Delta F$ at the corresponding temperatures are given in columns 2, 3, 4, and 5 respectively in Table II.

$N/\text{cm.}^2 = (p/T - p_1/T_1) \times 3{\cdot}359 \times 10^{18}$. $\theta = (p/T - p_1/T_1) \times 2824$.

The adsorbed film of water on a platinum surface the equilibrium pressure of which is equal to the vapour pressure of water is produced

TABLE II.

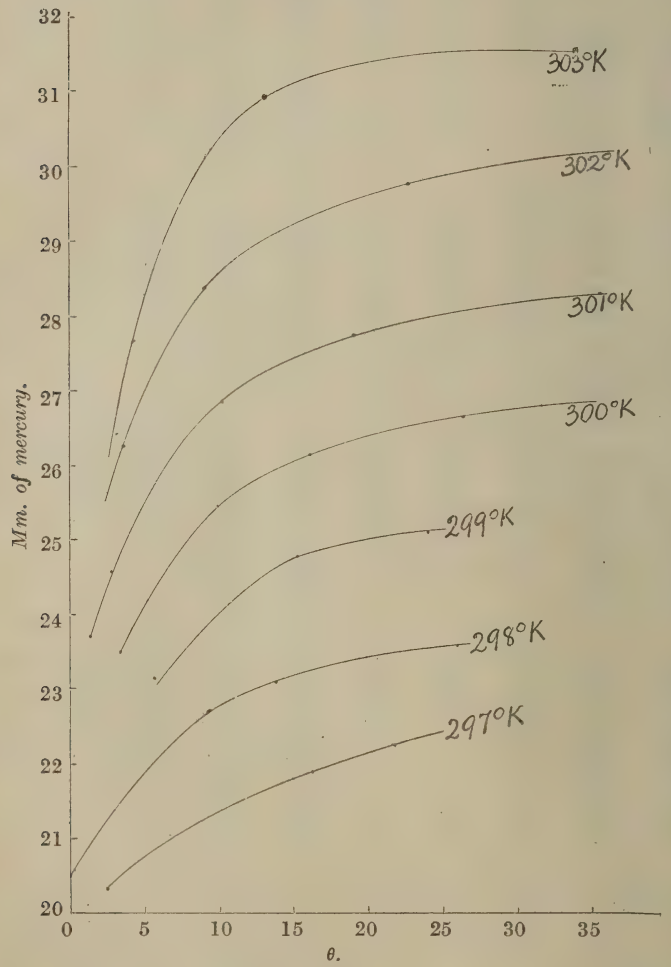
$T°$ abs.	p mm.	N/cm.^{2} $\times 10^{-14}$.	θ.	$-\Delta F$.	$T°$ abs.	p mm.	N/cm.^{2} $\times 10^{-14}$.	θ.	$-\Delta F$.
		No. 1.					No. 2.		
293·5	18·01	265·3	22·3	0·0	296·0	21·07	278·8	23·4	0·0
294·0	18·46	218·3	18·4	6·06	296·5	21·40	248·5	20·9	8·0
295·0	19·10	151·2	12·7	22·0	297·0	21·88	194·8	16·3	13·0
296·0	19·83	77·3	6·5	35·5	298·0	22·71	110·8	9·3	26·7
297·0	20·32	30·2	2·5	57·0	299·0	23·17	67·2	5·6	50·5
298·0	20·61	3·36	0·28	84·1	300·0	23·50	40·3	3·3	77·1
299·0	20·73	—	—	—	301·0	23·71	16·8	1·4	107·1
301·0	20·88	—	—	—	303·0	24·10	—	—	—
303·0	21·12	—	—	—	306·0	24·44	—	—	—
306·0	21·42	—	—	—	309·0	24·76	—	—	—
309·0	21·68	—	—	—	312·0	25·09	—	—	—
		No. 3.					No. 4.		
296·5	21·70	315·7	26·5	0·0	298·0	23·76	309·0	26·0	0·0
297·0	22·24	258·6	21·7	3·53	299·0	24·79	181·4	15·2	8·6
298·0	23·10	164·6	13·8	16·6	300·0	25·46	117·5	9·9	29·5
299·0	23·70	114·2	9·6	36·9	302·0	26·29	43·66	3·6	80·3
300·0	24·20	67·2	5·6	59·6	303·0	26·43	36·94	3·1	112·0
301·0	24·57	33·6	2·8	85·6	306·0	27·04	—	—	—
303·0	24·95	10·07	0·84	146·8	309·0	27·43	—	—	—
306·0	25·30	—	—	—	312·0	27·93	—	—	—
309·0	25·79	—	—	—					
312·0	26·10	—	—	—					
		No. 5.					No. 6.		
299·0	25·21	285·5	24·0	0·0	300·0	26·74	325·8	26·4	0·0
300·0	26·13	191·5	16·1	13·8	301·0	27·75	225·1	18·9	12·8
301·0	26·84	120·9	10·2	32·8	302·0	28·89	107·5	9·0	23·5
302·0	27·26	97·4	8·1	58·5	303·0	29·74	23·5	1·9	40·7
303·0	27·66	50·38	4·2	84·7	304·0	30·10	—	—	—
306·0	28·20	23·51	1·9	177·6	306·0	30·27	—	—	—
309·0	28·68	—	—	—	309·0	30·80	—	—	—
312·0	28·99	—	—	—	312·0	31·29	—	—	—
		No. 7.					No. 8.		
301·0	28·30	423·2	35·6	0·0	302·5	30·91	463·5	38·9	0·0
302·0	29·77	272·1	22·9	5·5	303·0	31·50	399·7	33·6	5·4
303·0	30·92	154·5	13·0	17·3	304·0	32·93	258·6	21·7	13·9
304·0	31·79	70·5	5·9	35·2	305·0	34·10	141·1	11·8	27·2
305·0	32·21	36·94	3·1	75·9	306·0	34·92	63·83	5·3	47·2
306·0	32·66	—	—	—	307·0	35·31	33·59	2·8	74·8
308·0	32·87	—	—	—	309·0	35·86	—	—	—
311·0	33·41	—	—	—	312·0	36·38	—	—	—
314·0	33·76	—	—	—	315·0	36·88	—	—	—
317·0	34·03	—	—	—	318·0	37·43	—	—	—

according to varying temperatures when from 265·3 to 325·8 $\times$ 10^{14} molecules are adsorbed per sq. cm. The curves in Fig. 4 show the change in the equilibrium pressure of the film with varying thickness at constant temperature. The limiting pressure value of adsorption measurements at any one temperature is the normal vapour pressure of water at that temperature. Hence the highest pressure on each isotherm is the vapour pressure of water at that temperature. It is evident from the shape of these isothermal curves that they will all cut the ordinate axis at a finite pressure. It follows that below

these pressures measurable adsorption of the type studied here does not occur. These pressures where the adsorption first begins cannot be measured directly, but the extrapolation of these curves

FIG. 4.

Platinum–water.



would give this pressure. The value so obtained from the 298°-isotherm is 20·50 mm. The isotherms above 298° abs. will cut the pressure axis above this point. The extrapolation of the other curves is unwarranted. It is possible that a stable film of adsorbed water is present on the platinum surface whose equilibrium pressure

is too small to be measured by this means. If this is actually the case, the true value of the molecular thickness would be $\theta + n$, where n is the number of molecular layers in the stable film. However, allowing for the possible existence of a stable film on the surface, we may still say that adsorption of the type studied here begins at a finite pressure.

The adsorption on glass is much greater than on platinum. The free energy change accompanying adsorption on a glass surface is much greater than that on a platinum surface.

The results given here are in good agreement with those of other investigators working at similar pressures and temperatures and with similar surfaces but by different methods.

The best of these are probably those of Ihmori (*loc. cit.*), who studied the adsorption of water on a plane Jena glass surface. He states the thickness of the adsorbed film on a glass surface to be from 0·3 to $4{\cdot}0 \times 10^{-6}$ cm. Our results show the film to be from 0·0 to $5{\cdot}3 \times 10^{-6}$ cm. thick. His value for platinum is from 0·0 to $1{\cdot}2 \times 10^{-6}$ cm., whilst ours is 0·0 to $1{\cdot}13 \times 10^{-6}$ cm. Other investigators, working with powdered substances or with glass wool, have obtained consistently higher values than these. These large adsorption values are due to the difficulties involved in calculating the surface of a finely-powdered substance and to capillary and sorption effects. As the adsorption measured here is a reversible equilibrium, it cannot be due to solid solution or chemical combination.

This work is being extended by one of us to other surfaces and vapours.

Summary.

(1) A new method has been devised for measuring the adsorption of vapours on solid surfaces.

(2) The adsorption of water vapour on a glass and a platinum surface has been studied.

(3) The number of molecules adsorbed per sq. cm. has been accurately determined and this value for an adsorbed film, the equilibrium pressure of which is equal to that of the vapour pressure of water, has been determined for glass and platinum surfaces.

(4) The change in free energy accompanying adsorption of water from the gaseous phase on glass and platinum surfaces at various temperatures and different numbers of molecules per sq. cm. adsorbed has been calculated.

(5) The magnitudes of the adsorption of water from the gaseous phase on glass and on platinum surfaces have been compared qualitatively.

(6) Experimental results show, in the case of water vapour on a platinum surface, that this type of adsorption begins at a finite pressure.

The authors wish to express to Prof. F. G. Donnan their appreciation of the interest he has taken in this research.

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CCIX.—*A New Method of Diagnosing Potential Optical Activity. Part I. The Optical Activity of Chlorobromomethanesulphonic Acid.*

By JOHN READ and ANN MORTIMER MCMATH.

THE difficulty of obtaining satisfactory experimental evidence of the actual or potential existence of optically active forms, corresponding with enantiomorphous modifications, of substances possessing fewer than three carbon atoms in the molecule is well known. Despite repeated attempts on the part of numerous investigators, the accounts of which have doubtlessly remained to a large extent unpublished, it was not until forty years after the promulgation of Le Bel and van 't Hoff's theory of the spatial molecular configuration of carbon compounds that incontrovertible proof was forthcoming of the capacity of substances of such simple molecular constitution to exist in optically active enantiomorphous modifications. Even yet, chloroiodomethanesulphonic acid, $CHClI{\cdot}SO_3H$, resolved into optically active components by Pope and Read in 1914 (J., **105**, 811), provides the sole example of the existence of a one carbon-atom molecule in optically active modifications. Since failure to resolve such simple asymmetrically constituted substances had been hitherto ascribed to their ready racemisation, the extraordinarily pronounced optical stability of the active forms of chloroiodomethanesulphonic acid (*loc. cit.*, p. 819) provided a striking and unexpected contrast to Swarts' description of the presumed immediate racemisation of fluorochlorobromoacetic acid when liberated from combination with strychnine (*Bull. Acad. roy. Belg.*, 1896, **31**, 28; "Mémoires couronnés," 1896, 54), and Porcher's account of the fleeting activity of chlorosulphoacetic acid (*Bull. Soc. chim.*, 1903, **27**, 438).

Many seeming anomalies remained after the optical resolution of chloroiodomethanesulphonic acid, one of the most striking being

the lack of success to resolve chlorobromomethanesulphonic acid (compare Pope and Read, J., 1908, **93**, 797). This substance bears the closest conceivable constitutional relationship to chloroiodomethanesulphonic acid, and also, as described below, forms a brucine salt distinguished by an almost identical sparing solubility. Nevertheless, repeated attempts to prepare optically active specimens of the bromo-acid or its salts by fractional precipitation with brucine, according to the method applied successfully to the iodo-acid, resulted in failure. In seeking a reason for this apparent anomaly, it appeared very improbable, in the light of the observations recorded for the iodo-acid, that any explanation could be based upon extreme facility of racemisation; but before exploring other lines of inquiry it was felt advisable to submit this possibility to more stringent tests than have been as yet applied in investigations of the kind. In further experiments with brucine and strychnine, the possible racemising action of heat and alkaline reagents was avoided as far as possible by producing the alkaloidal salts from aqueous solutions at the ordinary temperature and decomposing the various fractions with the minimum amount of cold dilute ammonia; no resolution, however, could be established in this way.*

In view of the possible catalytic racemising action of water upon a presumed highly mobile asymmetric system, attempts were next made to carry out the processes as completely as possible in organic solvents. The very sparing solubility of the brucine salt appeared unfavourable for such a purpose, and eventually hydroxyhydrindamine was selected as a base likely to yield a salt capable of ready fractional crystallisation from a suitable series of organic solvents (Pope and Read, J., 1912, **101**, 760). Preliminary experiments showed that no resolution could be accomplished by using this base in aqueous solution. The salt prepared by mixing equivalent amounts of the free acid and *l*-hydroxyhydrindamine in presence of acetone containing traces of water crystallised without difficulty, and exhibited two widely distinct kinds of crystals at the first recrystallisation from this solvent: a preliminary separation of compact, glistening plates was succeeded in the supernatant mother-liquor by a radiating mass of long, silky needles; and upon carrying out a lengthy fractional crystallisation these two forms recurred,

* These experiments, carried out at intervals over a long period but hitherto unpublished owing to the inconclusive results, were completed prior to the publication of the recent paper by Backer and Burgers (this vol., p. 233) describing the successful adoption of very similar precautions in the apparently partial optical resolution of chlorosulphoacetic acid. The chlorobromomethanesulphonic acid used in the preliminary work was kindly made available several years ago by Sir William Pope.

any particular fraction consisting as a rule of one type only. The plates, when carefully recrystallised from acetone, separated in magnificent and highly lustrous crystals of tabular habit; whilst the needles maintained their characteristics when recrystallised from glacial acetic acid: the description below indicates their widely different morphological characteristics. Further examination disclosed the remarkable fact that the needles when recrystallised from acetone of ordinary purity separated mainly in the tabular form, whilst the plates when recrystallised from glacial acetic acid yielded nothing but needles; moreover, both kinds of crystals decomposed at practically the same temperature (187°), although the tabular form exhibited a preliminary change in appearance well below this point (160°). The relationship would therefore be ascribed in the ordinary way to the occurrence of dimorphism; and, indeed, the general appearance of the two kinds of crystals in the original separation was strongly reminiscent of the dimorphic forms of *p*-bromoacetanilide, as pictured by Chattaway and Lambert (J., 1915, **107**, 1766). Upon fuller examination, however, the plates and needles, although both giving a molecular rotatory power in dilute aqueous solution equivalent to that of the basic ion, were found to display widely different rotatory powers in organic solvents. Further, the plates, which gave the higher numerical values, exhibited marked downward mutarotation * in these solvents, the final value being in each case practically identical with the value observed for the needles in the same solvent. No mutarotation was evident in aqueous solution. Of all the organic solvents available, the plates gave the highest numerical values in pure dry acetone; moreover, the needles, which otherwise displayed little tendency towards mutarotation, showed a rapid upward change in this solvent until the attainment of the final value given by the plates in the same solvent. In all instances, the crystalline residues obtained by ordinary evaporation of the above solutions on the water-bath gave the rotatory powers characteristic of the needles, when redissolved in the various solvents indicated.

After further investigations, described below, these results were interpreted by assuming that the plates and needles represent salts of *l*-hydroxyhydrindamine with *l*- and *dl*-chlorobromomethanesulphonic acid, respectively. The main measurements of molecular rotatory power may now be summarised in the following

* For the sake of brevity the term "mutarotation" is used throughout this paper to denote the observed progressive changes in rotatory power, although possibly it would be preferable to use a distinctive word for changes of the special nature here concerned.

table, in which the above salts are designated by the respective symbols *lBlA* and *lBdlA* :

Solvent.	Salt *lBlA*. Original $M[\alpha]_D$.	Salt *lBlA*. Final $M[\alpha]_D$.	Salt *lBdlA*. Original $M[\alpha]_D$.	Salt *lBdlA*. Final $M[\alpha]_D$.	Calculated $M[\alpha]_D$ for *lA*.	Calculated $M[\alpha]_D$ for *lBdA*.
Methyl alcohol (absolute)	−180°	−71°	−71°	−71°	−109°	+38°
Ethyl alcohol (99·5%)	−180	−90	−75	−83	−105	+30
Acetone (pure anhydrous) ...	−256	−187	−71	−187	−185	+114
Glacial acetic acid	−184	−66	−59	−59	−125	+ 66
Water	−60	−60	−60	−60	—	—

The values in water are practically coincident with the value ±60·5° recorded for the basic ion in dilute aqueous solution (J., 1912, **101**, 770).

It has been observed that the active hydroxyhydrindamines, more particularly in combination with weak acids, exhibit mutarotation in certain organic solvents (*loc. cit.*, p. 759); but the slight changes recorded below for *l*-hydroxyhydrindamine benzenesulphonate and *d*-hydroxyhydrindamine acetate disclose no similarity to the very sharply defined changes now under discussion. Further, the quantitative relationships explained below and the fact that marked differences persist in new salts prepared from the two *l*-hydroxyhydrindamine salts by displacement of the base do not permit of the mutarotation being referred to tautomeric change on the part either of the base or the acid.

In order to account for the experimental observations described in this paper we revert to the original view that asymmetric carbon compounds of simple molecular constitution are as a rule exceedingly susceptible to racemisation, owing to the mobility of the groups attached to the asymmetric atom. Moreover, we now advance the new idea, as applied to such compounds, that facile racemisation involves the complementary possibility of equally facile optical stabilisation, or " deracemisation," under appropriate conditions. Thus, a very labile asymmetric molecule, when submitted to a suitable asymmetric influence, will be transformed more or less completely into one of the two possible active modifications; but when the asymmetric influence is removed, the form present in excess will undergo auto-racemisation. In the example under notice, the most effective asymmetric influence yet discovered is provided by optically active hydroxyhydrindamine in acetone solution : the *l*-base transforms the *dl*-acid largely to *l*-acid, whilst the *d*-base transforms it in the same proportion to *d*-acid. An equilibrium is thus set up in the solution between

the diastereoisomeric salts *lBlA* and *lBdA* (or *dBdA* and *dBlA*), greatly to the advantage of the former. Upon dissolving the pure solid salt, *lBlA* (or *dBdA*), in various other organic solvents, a more or less rapid racemisation of the active acid occurs, resulting as a rule in the complete, or almost complete, conversion of the salt *lBlA* (or *dBdA*) into the partially racemic salt *lBdlA* (or *dBdlA*); moreover, it has been shown that the racemisation is accelerated remarkably by the addition of small quantities of water to the solvent. Thus, in 99·5% ethyl alcohol the downward mutarotation extended over a period of 23 hours, whereas in 90% ethyl alcohol it was complete in 12 minutes.

All the recorded observations were made at the ordinary temperature, and the only solvents submitted to special purification were methyl alcohol and acetone for use in making standard determinations of optical rotatory power. For purposes of recrystallisation, acetone of the purity necessary for ordinary analytical operations was used. More detailed observations, involving the use of carefully purified solvents at a constant temperature and a study of the effect of water and other catalysts, will be carried out in due course.

The results recorded for solutions in 99·5% ethyl alcohol and glacial acetic acid suggest that even in these solvents a state of equilibrium is attained between the salts *lBlA* and *lBdA*, which does not correspond with the presence of equimolecular proportions of the two salts. Thus, in 99·5% ethyl alcohol, the value of $M[\alpha]_D$ for the pure salt *lBlA* declined from $-180°$ to $-90°$, whilst the value for *lBdlA* rose from $-75°$ to $-83°$. Accepting $-90°$ as the equilibrium value, and $-180°$ as the value for the pure salt *lBlA*, this observation corresponds with an optical equilibrium mixture composed of 57% of *lBlA* and 43% of *lBdA*, or 14% of *lBlA* and 86% of *lBdlA*. The values observed in pure dry acetone solution leave no doubt as to the existence in this solvent of an equilibrium between the two diastereoisomeric salts, *lBlA* and *lBdA*, the former predominating considerably in amount. Equilibrium is attained in this solvent with great rapidity from either side. The salt *lBlA* showed a downward mutarotation from the original value $M[\alpha]_D = -256°$ until the attainment of the equilibrium value, $M[\alpha]_D = -187°$, in about an hour; on the other hand, the partially racemic salt, *lBdlA*, exhibited an upward mutarotation from the original value, $M[\alpha]_D = -71°$, to the same equilibrium value. The upward change appeared to take slightly longer than the downward one, but more refined measurements will be needed to establish this point definitely. The curves in Fig. 2 illustrate the main trend of these and other changes.

It is thus clear that in acetone solutions of the concentrations examined, the diastereoisomeric salts, *lBlA* and *lBdA* (or *dBdA* and *dBlA*), exist in dynamic equilibrium at the ordinary temperature in the proportion of about 81% of the former to 19% of the latter, and that by careful crystallisation the whole of the original *dl*-acid may be obtained in the form *lBlA* (or *dBdA*). In effect, although not strictly in accordance with definition, this result is tantamount to a partial asymmetric synthesis with complete theoretical efficiency. The following schemes represent (i) the usual course of events in the optical resolution of an externally compensated acid by a lævorotatory base, and (ii) the optical resolution of *dl*-chlorobromomethanesulphonic acid by *l*-hydroxyhydrindamine in acetone solution, under the conditions indicated :

$$\text{(i)}\quad \underset{}{2lB} + \underset{}{dAlA} = \underset{50\%}{lBlA} + \underset{50\%}{lBdA}.$$

$$\text{(ii)}\quad \underset{}{2lB} + \underset{}{dAlA} = \underset{81\%}{lBlA} \rightleftharpoons \underset{19\%}{lBdA}.$$

No displacement in the equilibrium was observed on diluting the solution in pure acetone from about 0·6 to 0·15%.

The progress of the separation of crystals of *l*-hydroxyhydrindamine *l*-chlorobromomethanesulphonate from a solution in ordinary acetone of *l*-hydroxyhydrindamine *dl*-chlorobromomethanesulphonate was traced by a periodical examination, during the crystallisation, of the salt remaining in the mother-liquor : the results showed that, in accordance with anticipation, the mother-liquor contained a large excess of the salt *lBlA* throughout the process. The lowest value observed for the residual dissolved salt was − 122°, corresponding with a mixture of 64% of *lBlA* with 36% of *lBdA*, notwithstanding the presence of traces of water in the acetone.

Owing to the insolubility of the salts in benzene, chloroform, etc., no observations have yet been practicable in non-miscible solvents. Neither of the salts exhibited any change in optical rotatory power when heated at 110° for 2 hours, but the salt *lBlA* showed a marked decline, indicative of partial racemisation, when kept at 160° for ½ hour. The tabular crystals of this salt lose their transparency when kept, but as yet no accompanying change in the rotatory power of the dissolved substance has been noticed.

By subtracting the molecular rotatory power of the salt *lBdlA* from that of the salt *lBlA*, determined in the same solvent under precisely similar conditions, a value is obtained for the molecular rotation exerted by the acid part of the molecule of the second salt; the values recorded in the fifth column of the above table were calculated in this way. The values given in the last column

for the salt *lBdA* have also been deduced algebraically from the values observed for the same two salts, listed respectively in the first and third columns. It is not desired to emphasise unduly the numerical significance of the values thus derived, nor to compare them in point of precision with ionic values; yet, in view of their common method of derivation, they afford an indication of the relative order of magnitude of corresponding molecular rotatory powers in different solvents. Moreover, results of great interest have been obtained by comparing the values for chlorobromomethanesulphonic acid with values derived in a similar way for chloroiodomethanesulphonic acid. For this purpose, determinations of the molecular rotatory powers, hitherto unavailable, of *d*- and *l*-hydroxyhydrindamine *d*-chloroiodomethanesulphonate were made in absolute methyl alcohol, glacial acetic acid, and acetone, in solutions having a concentration of about 1%. These two salts were prepared for the purpose from a specimen of barium *d*-chloroiodomethanesulphonate having $M[\alpha]_D = +37{\cdot}7°$ in 1% aqueous solution, and neither of the salts was purified by fractional crystallisation. No mutarotation was observed in any instance. The observed and derived values immediately concerned are tabulated below:

	$M[\alpha]_D$ of hydroxyhydrindamine salt of				$M[\alpha]_D$ derived for	
	Bromo-acid.		Iodo-acid.		Bromo-	Iodo-
Solvent.	*lBlA*.	*lBdlA*.	*dBdA*.	*lBdA*.	acid.	acid.
Methyl alcohol (absolute)	−180°	−71°	+122°	−35°	−109°	+44°
Glacial acetic acid	−184	−59	+118	−27	−125	+46
Acetone (pure) .	−256	−71	+192	−42	−185	+75

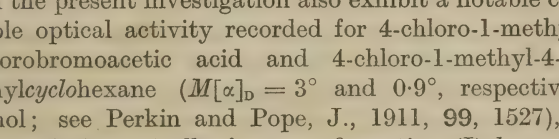
Thus, for both acids, the salts *dAdB* (or *lAlB*) yield the highest molecular rotatory power in acetone, whilst the values in methyl alcohol and acetic acid are considerably lower and practically identical in each instance for the two solvents. The ratio between the derived values of $M[\alpha]_D$ given in the last two columns is 2·5/1 in methyl alcohol, 2·7/1 in acetic acid, and 2·5/1 in acetone. Adopting a mean ratio 2·6/1, the calculated molecular rotatory power of the ion of chlorobromomethanesulphonic acid in dilute aqueous solution would thus be $M[\alpha]_D = \pm 98°$, based on the corresponding value observed for the ion of the iodo-acid, namely, $M[\alpha]_D = 37{\cdot}7°$, noted above.

Although chloroiodomethanesulphonic acid may not yet have been obtained optically pure, it is evident that a remarkable enhancement of molecular rotatory power attends the substitution of bromine for iodine in this simple molecule, and it will be a matter

of considerable interest to trace the quantitative optical effect of similar substitutions by means of a further application of the method now indicated.

The relationship just elucidated between the molecular rotatory powers of the hydroxyhydrindamine salts of these two acids appears even more striking when it is added that prior to making the above determinations of rotatory power for the salts of the iodo-acid we had failed to notice any downward mutarotation of *l*-hydroxyhydrindamine *l*-chlorobromomethanesulphonate when dissolved in acetone of ordinary purity. The constant value $M[\alpha]_D = -158°$, originally observed, was thus assumed to represent the molecular rotatory power of the pure salt *lBlA* in acetone. This value, taken in conjunction with the original value observed in the same solvent for the salt *lBdlA* (— 93°), led to the derived value $M[\alpha]_D = -64°$ for *lA*, whereas the above ratio 2·6/1 indicated $M[\alpha]_D = -194°$. It seemed likely, therefore, that the value for the pure salt *lBlA* was very much higher than $M[\alpha]_D = -158°$, and that the latter value had been attained through a rapid downward mutarotation to a point of equilibrium prior to polarimetric examination. By using scrupulously purified acetone and making the first polarimetric observation within 3 minutes of the first contact of solid with solvent, we were eventually successful in obtaining an initial value of $M[\alpha]_D = -256°$ for this salt, and in detecting the anticipated rapid fall to the equilibrium value; moreover, the initial value for the pure salt *lBdlA* was reduced in a similar way from — 93° to — 71°. The value of $M[\alpha]_D$ for *lA* thereby became — 186°, in place of the value — 64° first deduced, and thus approximated very closely to the anticipated value, — 194°.

The optical effect of configuration (I) thus appears to be numerically about 2·6 times as great as that of (II), and the high values observed in the present investigation also exhibit a notable contrast to the feeble optical activity recorded for 4-chloro-1-methyl*cyclo*hexyl-4-chlorobromoacetic acid and 4-chloro-1-methyl-4-chlorobromomethyl*cyclo*hexane ($M[\alpha]_D = 3°$ and 0·9°, respectively, in ethyl alcohol; see Perkin and Pope, J., 1911, **99**, 1527), which may be derived theoretically from configuration (I) by replacing the simple group SO_3H by a large complex radical, R (III) :



It is suggested that the low molecular rotatory powers exhibited by configurations (II) and (III) may be due largely to a steric

effect: comparing (I) and (II), the substitution of I for Br would leave less of the environment of the carbon atom available for H, Cl, and SO_3H; whilst, comparing (I) and (III), the substitution of R for SO_3H would lead to a still more pronounced curtailment of the space available for H, Cl, and Br. It will be interesting to investigate this idea further by the examination of other asymmetric substances of analogous constitution.

When separated from the optically active base, chlorobromomethanesulphonic acid racemises with extreme ease. Although the asymmetric influence of the base enables a distinctive crystalline β-naphthylamine salt to be isolated from *l*-hydroxyhydrindamine *l*-chlorobromomethanesulphonate, in admixture with β-naphthylamine dissolved in glacial acetic acid, the salt shows no optical activity immediately after solution in organic solvents, and when recovered from the solvent has undergone transformation into the β-naphthylamine salt deposited directly from a mixture of β-naphthylamine and *l*-hydroxyhydrindamine *dl*-chlorobromomethanesulphonate in glacial acetic acid.

Extremely interesting results were obtained by precipitating the various hydroxyhydrindamine salts by the addition of brucine acetate in acetone solution. The salt *lBlA* yielded a dextrorotatory brucine salt which gave a maximum original value of $[\alpha]_D = +6{\cdot}8°$ in glacial acetic acid solution, changing rapidly to a maximum lævorotation of $[\alpha]_D = -10{\cdot}4°$. The corresponding values for the brucine salt precipitated from the salt *lBdlA* were $-8{\cdot}0°$ and $-11{\cdot}2°$, respectively. The dextrorotation of the brucine salt *lBlA* was also established in acetone solution. Since it transpired that salts of brucine with inactive acids of closely related constitution evinced no measurable optical activity when dissolved in glacial acetic acid under similar conditions, the optical effects noticed in the above determinations must be ascribed to the chlorobromomethanesulphonic acid. Two important points then emerge. In the first place, the brucine salts, like the hydroxyhydrindamine salts, exhibit mutarotation, in this instance rising in a lævo-sense in glacial acetic acid; so that, unlike *l*-hydroxyhydrindamine, brucine appears to stabilise a pronounced excess of the lævo-modification of the acid in glacial acetic acid solution. Secondly, the exchange of bases appears to be accompanied by optical inversion on the part of the acid. In the latter event, it was anticipated that *d*-hydroxyhydrindamine *d*-chlorobromomethanesulphonate, although containing the dextrorotatory acid, would fail to yield a dextrorotatory brucine salt. A further experiment confirmed this supposition, the first value observed for this brucine salt being $[\alpha]_D = -6{\cdot}6°$, rising in 90 minutes to a maxi-

mum value of $-10{\cdot}0°$. These curious phenomena of optical inversion, reminiscent in some ways of the Walden change, will be submitted to further investigation; but, in general, polarimetric observations on the brucine salts are rendered difficult owing to their very sparing solubility, and consequent small optical rotation, even in glacial acetic acid. The application of heat is necessary to effect solution, and in all instances this process occasions mutarotation towards zero, since the active brucine salts lose their rotatory power completely when heated on the water-bath in glacial acetic acid solution for 2 or 3 hours. In the course of the investigation of the brucine salts of chlorobromomethanesulphonic acid, evidence was obtained indicating that the salt of the inactive acid is the least soluble of the various salts or mixtures of salts possible: it would therefore be impracticable in any case to resolve the acid by fractional precipitation with this base.

By using *d*-hydroxyhydrindamine the salts *dBdA* and *dBdlA* were readily prepared in a similar manner, and these were proved experimentally to be respectively enantiomorphous with the above-mentioned salts *lBlA* and *lBdlA*. By mixing equal weights of *dBdA* and *lBdlA* in absolute methyl alcohol, and thus annulling the optical rotation due to the basic portions of the molecules, it was possible to demonstrate a slowly fading optical activity on the part of the acid present. The first value observed, $M[\alpha]_D = +49°$, agrees well with the calculated value, $+108°/2$. Chlorobromomethanesulphonic acid is thus the simplest substance which has yet been proved capable of exhibiting optical activity in the amorphous condition. The activity vanished completely in 32 hours, the racemisation being much more rapid than in the case of the salt *dBdA* (or *lBlA*), in which a powerful restraint appears to be exerted on the process by the full equivalent of *d*- (or *l*-) base present.

According to the views which have now found mention, the production of two wholly racemic salts might be anticipated, one of which would separate on mixing either salt of the *d*-base with either salt of the *l*-base in acetone, and the other of which would be deposited by crystallising a similar mixture from glacial acetic acid. These expectations were realised, the first racemate, *lBlA* . *dBdA*, crystallising in glassy prisms, and the second, *lBlA*,*lBdA* . *dBdA*,*dBlA*, in short, glistening needles. Morphologically, the racemates resemble the component salts very closely, but are more soluble and have lower melting points.

Close parallels to the results now brought forward are to be discerned in the work of McKenzie and Smith (J., 1923, **123**, 1962; 1924, **125**, 1582) on catalytic racemisation. These authors have

shown, for example, that *l*-menthyl *d*-phenylchloroacetate, through the catalytic action of a drop of alcoholic alkali, passes into an equilibrium mixture containing a preponderating amount of *l*-menthyl *l*-phenylchloroacetate. They have also established (*Ber.*, 1925, **58**, 894) the directing influence of an optically active terpene group in converting a mixture of equal amounts of diastereoisomeric menthyl (or bornyl) esters quantitatively into a mixture of unequal amounts of the same esters; thus, the addition of a trace of alcoholic alkali to a mixture of equal quantities of *l*-menthyl *d*-phenylchloroacetate and *l*-menthyl *l*-phenylchloroacetate causes the latter ester to preponderate (57%) without any analytical separation having been effected. Similarly, in the present investigation it appears that water exerts a powerful catalytic action which in most solvents results in the final production of equal, or very nearly equal, amounts of the two diastereoisomeric salts, *lBlA* and *lBdA* (or *dBdA* and *dBlA*); in acetone solution, however, the equilibrium is displaced strongly in favour of the first salt, and the actual position of the equilibrium would appear to be influenced *inter alia* by the amount of water present. It seems likely that in all instances the asymmetric directing influence of the optically active hydroxyhydrindamine becomes operative through the interposition of a catalytic agent, which may well prove to be water, even in the carefully dried acetone used in making the more refined observations recorded herewith.

An example of the general principle we now outline for simple asymmetric carbon compounds is provided in the case of the asymmetric tin atom by the well-known investigations of Pope and Peachey on methylethylpropylstannonium *d*-camphorsulphonate and *d*-bromocamphorsulphonate: evaporation of aqueous solutions of these salts led in each instance to the deposition of the single substance, *dBdA*, owing to progressive racemisation of the salt remaining in the mother-liquor (P., 1900, **16**, 42, 116; compare also Mills and Bain, J., 1910, **97**, 1866). In the case of the active salts *lBlA* and *dBdA* now under consideration, a partly racemic salt of the type *l*(or *d*)*BdlA* was usually left upon evaporating solutions in acetone containing a little water, although under certain conditions an excess of the original salt was found in the residue. The deposited salts of the tin compound were, however, characterised by sparing solubility, whereas with the hydroxyhydrindamine chlorobromomethanesulphonates no deposition occurs from warm acetone containing small amounts of water until most of the solvent has volatilised. No evidence has been adduced of the stabilisation of an excess of one form of the optically active stannonium compound in solution, the mother-liquor of the salt

dBdA being apparently a solution of the partial racemate *dlBdA*; the solvent concerned in this instance, however, is water, which instantly racemises *d*- or *l*-chlorobromomethanesulphonic acid, even when combined with optically active hydroxyhydrindamine.

The conception of extreme mobility of the simple atoms or groups attached to an isolated carbon atom also accords with Le Bel's hypothesis of a similar mobility of groups in asymmetric quinquevalent nitrogen compounds of simple molecular constitution, and with the observations of A. Werner and others on the ready racemisation of asymmetric assemblages associated with isolated atoms of cobalt, chromium, etc. Further, it affords an explanation of the difficulties experienced in preparing optically active substances containing fewer than three carbon atoms in the molecule, and is in agreement with the fugitive optical activity in aqueous solution of chlorosulphoacetic acid and its salts, indicated by Porcher (*loc. cit.*) and recently demonstrated by Backer and Burgers (this vol., p. 233). Incidentally, the suggestion that the variations in rotatory power shown by different fractions of the normal *d*-hydroxyhydrindamine salt of this acid indicated its partial resolution is also upheld (Pope and Read, J., 1914, **105**, 814). We anticipate that asymmetric compounds containing two carbon atoms in the molecule will also display phenomena of the kind now described, and thus lend themselves to preparation for the first time in optically pure combinations by treatment with optically active bases in organic solvents. Through a systematic application of the method to asymmetric compounds of simple molecular constitution, it is hoped to gather much new information respecting the comparative mobility of groups in systems of the kind.

It seems worthy of note that in the case of the optically active tin derivatives prepared by Pope and Peachey, the two dextrorotatory acids employed each imposed a dextrorotatory orientation upon the asymmetric complex involved. Similarly, in the present investigation, dextrorotatory hydroxyhydrindamine gives rise to dextrorotatory chlorobromomethanesulphonic acid, whilst lævorotatory hydroxyhydrindamine and lævorotatory brucine each favour a lævorotatory configuration of the associated asymmetric system. It will be interesting to ascertain whether any generalisation is possible on this basis, especially in view of the fact, to which attention may be directed, that in the closely related process of partial asymmetric synthesis the optically active product exhibits in the great majority of instances the same sense of rotation as the directive asymmetric system. Thus, *l*-brucine hydrogen methylethylmalonate yields an excess of the *l*-valerate when heated

(Marckwald, *Ber.*, 1904, **37**, 349); *l*-menthyl benzoylformate upon reduction gives an excess of the *l*-mandelate, and upon treatment with magnesium methyl iodide an excess of *l*-phenylmethylglycollate; whilst from *l*-menthyl pyruvate a lævorotatory lactic acid may be prepared by reduction; moreover, the *l*-bornyl group sometimes exerts a less pronounced asymmetric influence than the more highly lævorotatory *l*-menthyl group (McKenzie, J., 1904, **85**, 1249; 1905, **87**, 1373; 1906, **89**, 365 and 688). The results now described afford a very definite indication of the profound influence which may be exerted by an optically active nucleus upon an associated potentially active system, and provide a close parallel to the quantitative partial asymmetric syntheses which appear to occur in nature. Moreover, in our opinion, substances possessing the readily controlled asymmetric mobility evinced by chlorobromomethanesulphonic acid are much more likely to be amenable to processes of complete asymmetric synthesis, accomplished in the absence of optically active material, than any asymmetric substances yet investigated with this object in view. We propose to submit this new idea to practical tests at a later stage in these investigations.

The enormous difference in optical stability between chlorobromomethanesulphonic acid and chloroiodomethanesulphonic acid could not have been predicted, and is difficult to explain. In both instances the great resistance offered to alkaline hydrolysis is worthy of remark. The distinction may possibly be determined to some degree by the greater atomic volume, lower mobility, and less active chemical nature of iodine as compared with bromine. Possibly also the different affinity value, evidenced by the formation of such derivatives as $Ph{\cdot}ICl_2$, has a bearing upon the matter. It is hoped to gather further evidence by an examination of the remaining dihalogenomethanesulphonic acids and various closely related substances.

In continuing this series of investigations, we reserve the application of the method described not only to compounds of the simple molecular constitution indicated above, but also to other types of organic derivatives which may be conceived to possess potential optical activity associated with high mobility of the asymmetric system and therefore unrecognisable by any of the methods hitherto utilised. The exceedingly delicate diagnostic method we now describe may well lead to the discovery of optical activity on the part of organic types which, like chlorobromomethanesulphonic acid, have as yet resisted all attempts at optical resolution.

Experimental.

Preparation of dl-*Chlorobromomethanesulphonic Acid.*—The crude barium salt was prepared in the manner described by Andreasch (*Monatsh.*, 1887, **7**, 159), by heating barium chlorosulphoacetate to 120—130° in a sealed tube for several hours with bromine (1 mol.) and a little water. Chloromethanesulphonic acid and other impurities were eliminated by taking advantage of the sparing solubility of brucine chlorobromomethanesulphonate. To a warm aqueous solution of the recrystallised barium salt was added a similar solution containing one-third the calculated quantity of brucine acetate or brucine hydrochloride. For an amount of salt corresponding to 30 g. of the acid a total volume of about 500 c.c. was found suitable. After keeping for several hours the crystalline separation of brucine salt was collected and washed well with cold water, whilst the filtrate was treated in a similar way with a like amount of brucine. Both separations consisted of pure brucine chlorobromomethanesulphonate; practically two-thirds of the original acid was obtained in this form, the remaining one-third being rejected. The *brucine* salt forms minute, glistening needles, which decompose at 275°. It is practically insoluble in all the ordinary solvents, the most favourable being boiling glacial acetic acid (Found: C, 47·6; H, 4·3. $C_{24}H_{28}O_7N_2ClBrS$ requires C, 47·7; H, 4·6%).

For purposes of further work the brucine salt was mixed with cold water and shaken with an excess of dilute ammonia, the brucine being extracted with chloroform; evaporation of the aqueous liquid furnished the pure ammonium salt. No optical activity could be established with specimens of the salt prepared in this way. The *ammonium* salt is freely soluble in water or alcohol and sparingly soluble in warm acetone. It is best crystallised from hot glacial acetic acid, in which it is moderately soluble; it forms glistening plates, m. p. 205° (decomp.) (Found: NH_3, 7·6, 7·7. $CH_5O_3NClBrS$ requires NH_3, 7·5%). When the salt was heated under reflux for 2 hours with an excess of 10% aqueous sodium hydroxide solution, hydrolysis occurred to a slight extent only, the proportion of halogen removed being less than 2% of the total amount present.

Treatment of dl-*Chlorobromomethanesulphonic Acid with* l-*Hydroxyhydrindamine in Acetone Solution.*—An aqueous solution containing 14·7 g. of pure *dl*-chlorobromomethanesulphonic acid was evaporated as completely as possible on the water-bath in an open dish. Upon covering the partly crystalline mass with acetone (15 c.c.) and stirring in solid *l*-hydroxyhydrindamine (10·4 g.; 1 mol.), a

thick homogeneous liquid was produced, and when the stirring was continued for a short time on the water-bath the whole mass suddenly crystallised. The slightly brown, crystalline mass weighed 25·1 g. when dry. It was very soluble in water, ethyl alcohol, or methyl alcohol, moderately soluble in boiling acetone, sparingly soluble in ethyl acetate, and practically insoluble in ether, benzene, chloroform, light petroleum, etc.

A solution of the dry product in boiling acetone of ordinary purity (about 275 c.c.) and a small quantity of methyl alcohol was filtered and allowed to crystallise. The crystalline separation which accrued overnight (11 g.) consisted mainly of large, well-defined, glistening plates, but the upper part of the mother-liquor was filled with long, radiating needles. The latter dissolved readily when the fraction was separated and warmed with acetone; the undissolved residue (5·4 g.) was composed entirely of plates, which when freshly dissolved in cold methyl alcohol to form a 2·5% solution gave $[\alpha]_D = -48{\cdot}2°$, whence $M[\alpha]_D = -173°$, calculated for hydroxyhydrindamine chlorobromomethanesulphonate. The combined mother-liquors were concentrated, and the ensuing crystalline separation was subjected to a prolonged systematic fractional crystallisation from hot acetone, to which a little methyl alcohol was added when necessary. As a result, two distinct kinds of fractions were obtained, one consisting of plates and the other of needles. The plates predominated in the earlier fractions, although occasionally these yielded needles. Mother-liquors which had been repeatedly concentrated yielded needles more frequently than plates, especially when it was found necessary to accelerate the deposition of crystals by the addition of ether. The bulk of the material from the fractionation was obtained in the form of plates, although of seventeen fractions eight consisted wholly of plates and seven wholly of needles. The two kinds of crystals showed little distinction in melting point, but possessed characteristic optical rotatory powers when dissolved in organic solvents. Ordinary methyl alcohol was used as solvent in all the preliminary determinations, and the following typical result may be quoted for the plates: 0·2573 g., dissolved in methyl alcohol and made up to 20·0 c.c. at the ordinary temperature, gave $\alpha_D = -1{\cdot}24°$ when examined at once in a 2-dcm. tube, whence $[\alpha]_D = -48{\cdot}2°$, and $M[\alpha]_D = -173°$, calculated for hydroxyhydrindamine chlorobromomethanesulphonate. Other determinations of $M[\alpha]_D$ recorded for similar fractions were $-176°$, $-172°$, $-173°$, and $-172°$. In the case of a typical fraction composed of needles, 0·2550 g. when dissolved and examined under similar conditions gave $\alpha_D = -0{\cdot}51°$, whence $[\alpha]_D = -20{\cdot}0°$, and $M[\alpha]_D = -72°$.

Of the results yielded by other fractions of the same kind, the following may be quoted as representative: $M[\alpha]_D = -72°$, $-73°$, $-72°$, and $-73°$. Of the seventeen fractions examined, only two gave intermediate values, namely, $M[\alpha]_D = -119°$ and $-92°$, respectively: both these fractions were obtained by evaporating the solvent to dryness on the water-bath and inoculating the warm liquid mass with a crystal of the higher rotatory power. The final mother-liquor was dark in colour, and upon evaporation yielded a dark and somewhat tarry residue. By conversion to brucine salt and subsequent careful treatment with cold dilute ammonia, a somewhat brown specimen (1 g.) of ammonium chlorobromomethanesulphonate was prepared from the final residue; this was optically inactive in 3·5% aqueous solution when examined polarimetrically in a 2-dcm. tube in sodium light.

For the reasons stated above, the plates and needles were regarded as the *l*-hydroxyhydrindamine salts of *l*-chlorobromomethanesulphonic acid and *dl*-chlorobromomethanesulphonic acid, respectively.

l-*Hydroxyhydrindamine* l-*Chlorobromomethanesulphonate*, $C_9H_{11}ON{\cdot}CHClBr{\cdot}SO_3H$.—The various fractions of this salt obtained in the course of the fractional crystallisation were mixed and recrystallised from warm acetone containing a small quantity of methyl alcohol. No difference was apparent in the properties of the substance after this treatment. Under the proper conditions the salt crystallises with remarkable facility and may be readily obtained in lustrous, tabular crystals, measuring up to 1 cm. in length. Through the courtesy of Mr. T. V. Barker, the following crystallographic description and goniometric characterisation of the substance have been kindly furnished by Miss Marie Bentivoglio, of the Department of Mineralogy, University of Oxford, to whom we express our grateful thanks:

"*l*-Hydroxyhydrindamine *l*-chlorobromomethanesulphonate forms colourless crystals which become opaque when kept for a few weeks. The habit is tabular, parallel to *a* (100); sometimes two *q* (011) faces are large and two prisms suppressed, so that the crystal appears polar.

"The crystals belong to the monoclinic system, and the elements are $a : b : c = 1{\cdot}3246 : 1 : 1{\cdot}0780$; $\beta = 114° 19'$.

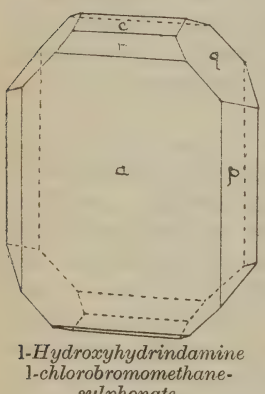
"The forms present are *a*, *p*, *c*, *r*, *q* (Fig. 1), and these have the following values:

	a (100).	*p* (110).	*c* (001).	*q* (011).	*r* (101).
ϕ.....	90° 0′	*39° 38′	90° 0′	23° 07′	90° 0′
.....	90 0	90 0	*24 19	*49 27	57 20 (16)

"Refractive index = 1·50."

l-Hydroxyhydrindamine *l*-chlorobromomethanesulphonate dissolves freely in water, or in methyl or ethyl alcohol at the ordinary temperature; it also dissolves readily in glacial acetic acid, and is moderately soluble in boiling acetone. It is very slightly soluble in hot ethyl acetate, but is practically undissolved by chloroform, benzene, ether, or light petroleum. It can only be recrystallised with certainty from warm acetone, to which the addition of a little methyl alcohol is permissible; as the solvent cools, the salt separates rapidly in the characteristic form, the initial deposition being facilitated in the case of a sterile solution by inoculation. When the acetone mother-liquors are allowed to evaporate to dryness in an open space at the ordinary temperature, the final separation usually consists mainly of needles of the partly racemic salt. In order to ascertain the relative stability of the two salts in contact with a saturated solution in ordinary purified acetone, a mother-liquor containing both plates and needles was kept in a desiccator, and after 3 days the needles had completely disappeared, whilst the plates had grown and maintained their lustre. *l*-Hydroxyhydrindamine *l*-chlorobromomethanesulphonate has a tendency to form supersaturated solutions, from which crystallisation takes place easily upon inoculation. Strong saturated solutions in warm methyl alcohol of ordinary purity redeposit the salt of the *l*-acid if cooled rapidly, but otherwise nothing but the partially racemic salt can be obtained from such solutions. In warm glacial acetic acid the salt of the *l*-acid is more readily soluble than the partially racemic salt, and a rapid and apparently complete conversion of the first-named salt to the second occurs in this solvent. When heated in a capillary tube, powdered *l*-hydroxyhydrindamine *l*-chlorobromomethanesulphonate loses its opacity at about 160° and decomposes at about 183° (Found: C, 33·8; H, 3·5. $C_{10}H_{13}O_4NClBrS$ requires C, 33·5; H, 3·6%).

FIG. 1.



l-Hydroxyhydrindamine l-chlorobromomethanesulphonate.

The optical rotatory powers of freshly made solutions of *l*-hydroxyhydrindamine *l*-chlorobromomethanesulphonate in the solvents utilised in the course of this investigation are summarised in the following table. The solutions were prepared as quickly as practicable, and heating was avoided if possible. With glacial acetic acid, and also with acetone at the higher concentration noted, it was found necessary, however, to warm the solvent on the water-

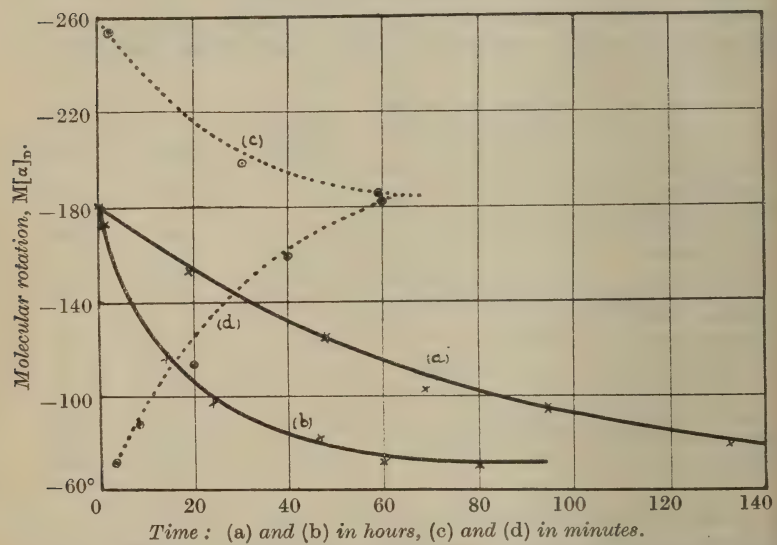
bath in order to effect solution. The interval which elapsed between the first contact with the solvent and the initial polarimetric observation was therefore appreciably longer in these two instances than in the others. The absolute methyl alcohol was dehydrated by means of metallic magnesium in presence of a trace of iodine (compare *Ber.*, 1923, **56**, 894). The "absolute" ethyl alcohol used contained about 0·5% of water. The acetone used for the original determination was of the purity required for ordinary analytical operations; but for the more dilute solutions very pure acetone was employed, which had been liberated from the sodium bisulphite compound and carefully dried and redistilled. The last-named solutions were prepared as rapidly as possible by shaking the finely powdered salt with the solvent at the ordinary temperature.

Solvent.	Approximate weight (g.) of salt in 20·0 c.c.	Time (minutes).	$[\alpha]_D$.	$M[\alpha]_D$.
Methyl alcohol (ordinary)	0·25	5	−48·6°	−174°
Methyl alcohol (absolute)	0·25	5	−50·0	−180
Ethyl alcohol (99·5%)	0·25	5	−50·0	−180
Acetone (ordinary)	0·25 (warmed)	30	−43·9	−158
Acetone (pure anhydrous)	0·10	20	−52·0	−187
Acetone (pure anhydrous)	0·05	10	−60·1	−216
Acetone (pure anhydrous)	0·025	3	−71·4	−256
Glacial acetic acid	0·25 (warmed)	10	−51·2	−184
Water	0·25	5	−16·9	− 60

All the solutions except those in water and acetone of ordinary analytical purity, which maintained their initial rotatory powers, exhibited marked downward mutarotation when kept at the ordinary temperature. The following typical series of values, selected from a mass of similar data, are sufficient to indicate the course of the changes. In methyl alcohol of ordinary purity, the initial molecular rotatory power of − 174° declined to − 115° in 14 hours, to − 97° in 24 hours, and reached a constant value of − 71° in 60 hours [Fig. 2 (*b*)]. In absolute methyl alcohol, the original value of − 180° fell to − 126° in 48 hours, − 102° in 70 hours, − 95° in 94 hours, − 86° in 146 hours, − 83° in 170 hours, and reached a constant value of − 71° in 220 hours [Fig. 2 (*a*)]. In absolute ethyl alcohol, the original value of − 180° declined to − 96° in 15 hours, and attained a final value of − 90° in 23 hours. In glacial acetic acid, the original value of − 184° fell to − 96° in 17 hours, and reached a constant value of − 66° in 35 hours.

Of these solvents, by far the slowest change thus occurred in absolute methyl alcohol. No mutarotation was apparent in a solution prepared by dissolving about 0·25 g. of the salt in warm acetone of ordinary purity, a constant value of $M[\alpha]_D = -158°$ being obtained. More dilute solutions prepared rapidly at the ordinary temperature in pure anhydrous acetone exhibited a strikingly rapid downward mutarotation to a constant value of $M[\alpha]_D = -187°$ [Fig. 2 (c)]. The most dilute solution indicated in the above table gave $M[\alpha]_D = -256°$ after 3 minutes, sinking to

FIG. 2.



Mutarotation of 1-*hydroxyhydrindamine chlorobromomethanesulphonates:* (a) lBlA *in absolute methyl alcohol,* (b) lBlA *in ordinary methyl alcohol,* (c) lBlA *in pure acetone,* (d) lBdlA *in pure acetone.*

$-198°$ in 35 minutes, and reaching the equilibrium value, $-187°$, in somewhat less than an hour; whilst the solution of twice this concentration gave $M[\alpha]_D = -216°$ 10 minutes after the first contact with the solvent, and $-188°$ after 45 minutes.

Upon removing the volatile solvents on the water-bath at any stage during the change, without attempting to exclude traces of water, the residue was found to consist wholly of the partly racemic salt, with a molecular rotatory power of about $-72°$ in ordinary methyl alcohol. In one instance, a residue obtained in this way from methyl alcohol was induced to crystallise on the water-bath by inoculation with a trace of the tabular form of crystal: the

molecular rotatory power of the residue thereby rose to $-87°$. The striking difference in the velocity of mutarotation exhibited by solutions in ordinary and carefully dried methyl alcohol led to an investigation of the effect upon the process of adding small quantities of water to ethyl alcohol used as a solvent in similar determinations. Such additions proved to exert a very remarkable accelerating influence upon the change. In a typical determination, 0·2500 g. of the salt when dissolved in cold 90% ethyl alcohol gave $\alpha_D = -0·79°$ 4 minutes after the first contact with the solvent, whence $[\alpha]_D = -31·6°$ and $M[\alpha]_D = -113°$. Owing to the very rapid fall in rotatory power, a second reading could not be taken conveniently until a further period of 4 minutes had elapsed, when the value observed was $\alpha_D = -0·45°$. A constant reading, $\alpha_D = -0·43°$, was reached 12 minutes after the first contact: the final value of $[\alpha]_D$ was thus $-17·2°$, and of $M[\alpha]_D$ $-62°$. A specimen of the pure powdered salt, after keeping at 160° for 30 minutes, gave $M[\alpha]_D = -149°$ when freshly dissolved in absolute methyl alcohol.

l-*Hydroxyhydrindamine* dl-*Chlorobromomethanesulphonate*.—The various fractions of the needle-shaped crystals deposited during the original series of recrystallisations were purified by a further recrystallisation from hot glacial acetic acid. Upon cooling, the solvent deposited rosettes of hard, glittering needles, which were collected and washed with ethyl acetate; further preparations of the substance were made by dissolving the tabular crystals in the same solvent, when the separation formed on cooling consisted entirely of the partially racemic salt. The crystals, which are unsuitable for goniometric examination, show straight extinction with strong double refraction. The refractive index is greater than 1·60.

The salt is much more soluble in acetone and in methyl and ethyl alcohol than the salt of the *l*-acid, and is also slightly soluble in boiling chloroform. It is practically insoluble in benzene, ether, or light petroleum. In glacial acetic acid it dissolves with greater difficulty than the isomeric salt; crystallisation occurs with great ease from this solvent, and the substance shows no tendency to form supersaturated solutions. It dissolves sparingly in boiling ethyl acetate, and separates in fine needles upon cooling. When a solution of the salt in a little hot glacial acetic acid is diluted with hot ethyl acetate the liquid gradually becomes filled with magnificent interlacing aggregates, composed of long, silky needles radiating from centres: this procedure affords the best method of purifying the substance. Moderately strong solutions of the partially racemic salt in acetone readily deposit the characteristic tabular crystals

of *l*-hydroxyhydrindamine *l*-chlorobromomethanesulphonate when allowed to cool. *l*-Hydroxyhydrindamine *dl*-chlorobromomethanesulphonate decomposes at 187° without the preliminary change noticed in the case of the other salt (Found: C, 33·7; H, 3·7. $C_{10}H_{13}O_4NClBrS$ requires C, 33·5; H, 3·6%).

Optical rotatory powers were determined in various solvents, under the conditions outlined for the isomeric salt, the concentration being approximately 0·25 g. of salt in 20·0 c.c. of solution; the resulting values agreed very closely with the corresponding values furnished by the salt of the *l*-acid after the completion of the mutarotative changes. The partially racemic salt exhibited no mutarotation in methyl alcohol, glacial acetic acid, or water. A slight upward mutarotation occurred in 99·5% ethyl alcohol, until the final value given by the isomeric salt was practically attained: the initial value, $M[\alpha]_D = -75°$, rose in 4 hours to $-80°$, and in 20 hours to $-83°$, and no further change was observed.

Very striking changes were traced in acetone solutions. In a preliminary series of observations, about 0·25 g. of the salt was dissolved in acetone of ordinary purity, by warming for 10 minutes on the water-bath and then making up the cooled solution to 20·0 c.c. with the solvent: the original molecular rotatory power of $-93°$ rose in 20 hours to $-147°$, and in 27 hours to a constant value of $-154°$. When evaporated to dryness on the water-bath, the solution yielded a crystalline residue which exhibited a molecular rotatory power of $-104°$ when freshly redissolved in acetone; after 20 hours the value had again risen to $-154°$, at which it remained constant. In a similar experiment, the residue recovered by evaporation on the water-bath gave an original value of $-148°$ when freshly dissolved in methyl alcohol; after 40 hours, the molecular rotatory power had declined to a constant value of $-74°$. When dissolved in 90% ethyl alcohol, this salt gave a constant molecular rotatory power of $-63°$.

A much more rapid upward mutarotation occurred in pure anhydrous acetone: 0·1014 g. of the salt, dissolved to 20·0 c.c., gave $[\alpha]_D = -18°$, 3 minutes after the first contact with the cold solvent, whence $M[\alpha]_D = -71°$. The successive values observed after 8 minutes and 20 minutes, respectively, were $M[\alpha]_D = -89°$, and $-124°$; the constant value, $-187°$, attained in about an hour, is identical with the equilibrium value furnished by the isomeric salt under similar conditions [Fig. 2 (d)]. The main relationships between the molecular rotatory powers displayed by the two isomeric salts in various solvents are summarised in the following table:

Solvent.	*l*-Hydroxyhydrindamine *l*-chlorobromomethane-sulphonate. Original $M[\alpha]_D$.	Final $M[\alpha]_D$.	*l*-Hydroxyhydrindamine *dl*-chlorobromomethane-sulphonate. Original $M[\alpha]_D$.	Final $M[\alpha]_D$.
Methyl alcohol (ordinary)	−174°	−71°	−72°	−72°
Methyl alcohol (absolute)	−180	−71	−71	−71
Ethyl alcohol (99·5%)	−180	−90	−75	−83
Ethyl alcohol ... (90%)	−113	−62	−63	−63
Acetone (ordinary)	−158	−158	−93	−154
Acetone (pure anhydrous) ...	−256	−187	−71	−187
Glacial acetic acid	−184	−66	−59	−59
Water	−60	−60	−60	−60

For the reasons already stated, a further examination was made into the nature of the process whereby the salt of the *dl*-acid after solution in acetone yields a separation of the isomeric salt of the *l*-acid. The partially racemic salt (4·4 g.) was dissolved in warm acetone of ordinary purity with the addition of a few drops of methyl alcohol, and upon allowing the solution to cool, a separation consisting wholly of tabular crystals was deposited. After the lapse of 50 minutes 5 c.c. of the clear mother-liquor were withdrawn, diluted to 20·0 c.c. with acetone, and examined polarimetrically in a 2-dcm. tube. By subsequently evaporating a measured portion of the diluted solution it was ascertained that the observed reading, $\alpha_D = -1{\cdot}02°$, corresponded to 0·2748 g. of the salt dissolved in 20·0 c.c. of acetone, whence $M[\alpha]_D = -131°$. After a further interval of 200 minutes, during which nothing but tabular crystals separated, 5 c.c. of the mother-liquor were found to contain 0·1790 g. of dissolved salt having a molecular rotatory power of −122°. It appears, therefore, that the solution in acetone always contains an excess of the salt *lBlA*, notwithstanding its continuous withdrawal during the process of crystallisation.

For purposes of comparison in two kinds of solvents giving rise to mutarotation, a specimen of l-*hydroxyhydrindamine benzenesulphonate* was prepared by mixing equivalent amounts of the free acid and base on the water-bath in presence of acetone containing a little water. The resulting crystalline solid separated from hot acetone containing a little methyl alcohol in clusters of glittering, anhydrous prisms, m. p. 198°, when the solution was allowed to cool (Found: C, 58·7; H, 5·7. $C_{15}H_{17}O_4NS$ requires C, 58·6; H, 5·5%).

The original molecular rotatory power of this substance in acetone

was — 140°, and a slight decline to a constant value of — 131° occurred in 20 hours. The salt recovered by evaporation on the water-bath gave a constant molecular rotatory power of — 75° in methyl alcohol. The original salt gave an initial value of — 100° in the same solvent, declining to a constant value of — 76° in 8 hours. A slight downward mutarotation was thus displayed in both types of solvent. *d*-Hydroxyhydrindamine acetate (J., 1912, **101**, 777) gave the constant value $M[\alpha]_D = + 61°$ in methyl alcohol, and in acetone declined from + 414° to + 382° in 44 hours.

Replacement of the Base in l-*Hydroxyhydrindamine* l- *and* dl-*Chlorobromomethanesulphonate.*—1. When *l*-hydroxyhydrindamine *l*-chlorobromomethanesulphonate was dissolved in warm acetone containing a trace of methyl alcohol and mixed with a solution of the calculated amount of brucine acetate in warm acetone, there was an immediate separation of well-defined crystalline needles. These were collected and washed with acetone, cold water, and again with acetone; the dry product represented an almost theoretical yield of brucine chlorobromomethanesulphonate. Owing to the sparing solubility of the salt, the determination of its optical rotatory power presented considerable difficulty; but readings were eventually obtained in acetone, which dissolves it slightly, and glacial acetic acid, which is the best solvent available for the purpose. A small quantity of the salt was heated on the water-bath for 20 minutes with acetone, so that a portion remained undissolved; after keeping for 24 hours at the ordinary temperature, the clear saturated solution gave $\alpha_D = + 0{\cdot}11°$ when examined polarimetrically in a 4-dcm. tube. In a further experiment, 0·1025 g. was completely dissolved in glacial acetic acid by heating on the water-bath for 25 minutes. The cold solution, when made up to 20·0 c.c. and examined forthwith in a 2-dcm. tube, gave $\alpha_D = + 0{\cdot}07°$, whence $[\alpha]_D = + 6{\cdot}8°$. A similar determination made upon a solution containing 0·2010 g. of the salt in 30·0 c.c. yielded the value $\alpha_D = + 0{\cdot}16°$ in a 4-dcm. tube. In a third determination an identical value was observed 15 minutes after the first contact with the solvent, but in 3 hours the solution exhibited no appreciable optical activity, and further readings were rendered impossible through the separation of crystals in the polarimeter tube. In a fourth determination, made upon a new preparation of the brucine salt, the initial value, $[\alpha]_D = + 6{\cdot}1°$, declined to zero in 45 minutes, to — 7·5° in 1·5 hours, and reached a constant value of — 10·4° in 3·5 hours; in this instance no crystallisation occurred. A fifth solution of the same kind when heated on the water-bath for 3 hours showed no appreciable optical activity in a 4-dcm. tube.

l-Hydroxyhydrindamine *dl*-chlorobromomethanesulphonate also yielded a brucine salt when treated in the manner described above; the two brucine salts were very similar in appearance, except that the second one crystallised in smaller needles than the first. A saturated solution of the second salt in acetone, prepared at the same time and in exactly the same manner as the corresponding solution of the first brucine salt, gave the value $\alpha_D = -0{\cdot}02°$ when examined polarimetrically in a 4-dcm. tube. This value, although difficult to establish with precision, is obviously different from the corresponding value, $\alpha_D = +0{\cdot}11°$, recorded above for the related salt. A solution of 0·1118 g. in glacial acetic acid, prepared in the manner described above and examined forthwith, gave $\alpha_D = -0{\cdot}13°$ in a 2-dcm. tube, whence $[\alpha]_D = -11{\cdot}2°$. In a second similar determination, 0·2010 g. made up to 30·0 c.c. with glacial acetic acid gave $\alpha_D = -0{\cdot}28°$ in a 4-dcm. tube, whence $[\alpha]_D = -10{\cdot}4°$. A third determination, made upon a new preparation of the brucine salt, gave an original value of $[\alpha]_D = -8{\cdot}0°$, which changed in the course of 9 hours to a constant value of $-10{\cdot}5°$. A fourth similar solution displayed no measurable optical activity after heating for 3 hours on the water-bath.

In several instances the brucine salt derived from *l*-hydroxyhydrindamine *l*-chlorobromomethanesulphonate crystallised from glacial acetic acid in the polarimeter tube, but no such behaviour was observed on the part of the second brucine salt, which thus appears to be the more soluble, or, at least, to have passed through the stage of the mutarotation corresponding to the least solubility.

Brucine *dl*-chlorobromomethanesulphonate, prepared by mixing aqueous solutions of equimolecular amounts of ammonium *dl*-chlorobromomethanesulphonate and brucine hydrochloride, dissolved with greater difficulty in hot glacial acetic acid than either of the brucine salts described above. When prepared by heating over a small flame and then examined immediately after cooling, a 0·5% solution showed no measurable optical rotation in a 2-dcm. tube, and the crystallisation of the substance in the tube rendered further observation impracticable. The various preparations of brucine salt obtained by fractional precipitation from aqueous solution showed similar behaviour when dissolved in glacial acetic acid, and thus consisted probably of brucine *dl*-chlorobromomethanesulphonate, as indicated below.

The optical inversion noticed upon precipitating *l*-hydroxyhydrindamine *l*-chlorobromomethanesulphonate with brucine acetate led to an examination of the optical rotatory power of the brucine salt prepared from an optically impure specimen of ammonium *l*-chloroiodomethanesulphonate, having $M[\alpha]_D = -28°$ in 1%

solution in glacial acetic acid. The brucine salt obtained by completely precipitating an aqueous solution of this ammonium salt by the addition of brucine hydrochloride had $M[\alpha]_D = -50°$ when dissolved to form a 0·6% solution in glacial acetic acid. No inversion was therefore apparent, and neither of these salts showed mutarotation in glacial acetic acid.

An investigation of a number of salts of brucine with optically inactive acids showed that such salts, when dissolved in glacial acetic acid to form solutions of the approximate molecular concentration indicated above, gave no measurable rotation when examined in a 4-dcm. tube in sodium light. The salts examined comprised brucine *dl*-chloroiodomethanesulphonate, brucine sulphate, and brucine benzenesulphonate. As a check, it was noted that the specimen of brucine sulphate used was appreciably active in 1% aqueous solution, the values observed being $[\alpha]_D = -24·4°$, and $M[\alpha]_D = -121°$ (Found: SO_4, 9·63; loss at 115° in 30 hours, 11·16. $B_2,H_2SO_4,6H_2O$ requires SO_4, 9·66; H_2O, 10·88%). *Brucine benzenesulphonate*, prepared by mixing the acid and base in presence of water and evaporating to dryness, crystallises from hot methyl alcohol, in which it is moderately soluble, in rosettes of glistening, anhydrous needles.

2. Of the many attempts made to replace the *l*-hydroxyhydrindamine in the above salts by an optically inactive base, avoiding water as a solvent, success was only achieved with benzidine and β-naphthylamine. Upon dissolving either of the *l*-hydroxyhydrindamine salts, with very gentle warming, in about ten times the weight of glacial acetic acid and adding at once to the cooled solution an equivalent quantity of benzidine dissolved in a like volume of the same solvent, an immediate and practically quantitative precipitation of the corresponding benzidine salt occurred. In each instance the salt consisted of minute needles, practically insoluble in water, acetone, or glacial acetic acid, and only slightly soluble in alcohol. About 0·1 g. of each salt was dissolved separately in absolute methyl alcohol on the water-bath, the cold solution being then made up to 20·0 c.c. with the solvent. About 10 minutes elapsed between first contact of the material with the solvent and the polarimetric observation, and no optical activity was observed in either instance.

3. The β-naphthylamine salts were prepared in a similar way, except that smaller amounts of glacial acetic acid were used. The β-naphthylamine salt obtained from *l*-hydroxyhydrindamine *l*-chlorobromomethanesulphonate was a crystalline powder, consisting of minute, glistening prisms, m. p. 210—240° (decomp.). The β-naphthylamine salt prepared from *l*-hydroxyhydrindamine *dl*-chloro-

bromomethanesulphonate was quite distinct in appearance from the salt just described: it consisted of well-defined, silky needles, which decomposed very definitely at 240°, without undergoing any preliminary change. The distinctions were confirmed by carrying out a second preparation of each salt. Neither of the β-naphthylamine salts was soluble in benzene or chloroform, but both were readily soluble in cold acetone or alcohol, and moderately soluble in warm glacial acetic acid. The salt obtained from the *dl*-acid appeared to be less soluble than the other, and either salt upon recrystallisation from glacial acetic acid yielded silky needles decomposing at 240°.

In each case, 0·15 g. of the original β-naphthylamine salt, when dissolved in cold acetone and made up to 20·0 c.c. with the solvent, failed to reveal any optical activity when examined polarimetrically in a 2-dcm. tube 5 minutes after the first contact with the solvent. A similar result was obtained by dissolving 0·2 g. in absolute methyl alcohol in an exactly similar manner. The residues recovered from the acetone and methyl alcohol solutions by allowing the solvent to evaporate at the ordinary temperature were identical in appearance.

d-*Hydroxyhydrindamine* d-*Chlorobromomethanesulphonate.*—A crystalline mass was readily obtained by mixing equivalent quantities of *d*-hydroxyhydrindamine and *dl*-chlorobromomethanesulphonic acid on the water-bath in presence of a little acetone, as described above for the *l*-base. When the product was recrystallised from warm acetone containing a little methyl alcohol, it yielded glistening plates, identical in appearance with crystals of *l*-hydroxyhydrindamine *l*-chlorobromomethanesulphonate: 0·2000 g. dissolved in absolute methyl alcohol at the ordinary temperature and made up to 20·0 c.c., gave $\alpha_D = +1{\cdot}00°$, when examined at once in a 2-dcm. tube, whence $[\alpha]_D = +50{\cdot}0°$, and $M[\alpha]_D = +180°$. The two salts crystallising in tabular form are thus enantiomorphously related. When the above solution was evaporated to dryness on the water-bath, the residue gave $M[\alpha]_D = +71°$ when redissolved in absolute methyl alcohol: the analogy between the enantiomorphous salts is thus complete.

The brucine salt derived from *d*-hydroxyhydrindamine *d*-chlorobromomethanesulphonate by precipitation in acetone solution was not noticeably different in appearance or solubility from the brucine salt derived in a similar way from the enantiomorphous substance. In this instance, however, no dextrorotation could be established by dissolving the brucine salt in glacial acetic acid: 0·1510 g., when dissolved in a few minutes by heating the solvent over a small flame and examined forthwith in the usual way, gave $\alpha_D =$

$-0{\cdot}10°$ in a 2-dcm. tube, whence $[\alpha]_D = -6{\cdot}6°$. A constant value of $[\alpha]_D = -10{\cdot}0°$ was attained after an interval of 90 minutes.

d-*Hydroxyhydrindamine* dl-*Chlorobromomethanesulphonate*.—The acetone mother-liquor from the salt just described was evaporated to dryness on the water-bath and the residue recrystallised from a small quantity of hot glacial acetic acid, with the addition of hot ethyl acetate in excess: the resulting long, silky needles gave a constant value of $M[\alpha]_D = +71°$ when dissolved in absolute methyl alcohol at the usual concentration, and exhibited the expected upward mutarotation when dissolved in acetone.

Wholly Racemic Forms of Hydroxyhydrindamine Chlorobromomethanesulphonate.—A solution of a mixture of equal weights of *l*- and *d*-hydroxyhydrindamine *dl*-chlorobromomethanesulphonate in a small amount of hot glacial acetic acid was diluted with hot ethyl acetate and allowed to cool. The crystalline separation which gradually ensued consisted wholly of rosettes of short, glistening needles. The substance, which was optically inactive, softened slightly at 155°, melted without decomposition at 175°, and recrystallised on cooling. In appearance it was very similar to *l*- or *d*-hydroxyhydrindamine *dl*-chlorobromomethanesulphonate, but was more soluble than these salts. The same substance resulted when a mixture of equal weights of *d*-hydroxyhydrindamine *d*-chlorobromomethanesulphonate and *l*-hydroxyhydrindamine *l*-chlorobromomethanesulphonate was treated similarly.

Upon crystallising the last-named mixture from acetone, in place of acetic acid, the resulting crystalline deposit contained the form of racemate just described, interspersed with large, glassy, transparent prisms, very similar in appearance to the original salts. These crystals, which melted at 160° and recrystallised on cooling, represented a second completely racemic form. A similar mixed deposit of needles and large prisms was also obtained by recrystallising the first racemic form from acetone. The interconversions shown by the constituent optically active salts thus persist in the racemates.

Exhibition of Optical Activity by Chlorobromomethanesulphonic Acid in Combination with an Optically Inactive Base.—Although no optical activity could be established when *l*(or *d*)-hydroxyhydrindamine in combination with *l*(or *d*)-chlorobromomethanesulphonic acid was replaced by a new optically inactive base, it was found that the optical activity of the acid in these salts persisted for a while when the activity of the combined hydroxyhydrindamine was neutralised by the addition of an equal weight of the salt containing the opposed optical form of this base in combination with the racemic acid. As an example, a mixture of

0·2024 g. of *d*-hydroxyhydrindamine *d*-chlorobromomethanesulphonate with 0·2024 g. of *l*-hydroxyhydrindamine *dl*-chlorobromomethanesulphonate was dissolved in cold absolute methyl alcohol and made up to 20·0 c.c. with the solvent. When examined in a 2-dcm. tube, 2 minutes after the first contact, an optical rotation of $\alpha_D = +0{\cdot}55°$ was observed, whence $[\alpha]_D = +13{\cdot}6°$, and $M[\alpha]_D = +49°$. In 4·5 hours the value of $M[\alpha]_D$ had declined to + 33°, in 7·25 hours to + 31°, in 28 hours to + 8°, and in 32 hours the optical activity had completely disappeared. The rate of change was thus considerably more rapid than that exhibited in the later stages of the mutarotation of *l*-hydroxyhydrindamine *l*-chlorobromomethanesulphonate in the same solvent.

The investigation will be extended, as occasion permits, in the various directions indicated. We express our acknowledgments to the Department of Scientific and Industrial Research for a maintenance grant to one of the authors (A.M.M.).

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CCX.—*The Nitration of* m-*Chlorophenol.*

By Herbert Henry Hodgson and Francis Harry Moore.

The scanty literature on this subject prior to 1924 deals only with 3-chloro-6-nitrophenol (Laubenheimer, *Ber.*, 1876, **9**, 76; Uhlemann, *Ber.*, 1878, **11**, 1161), 3-chloro-4 : 6-dinitrophenol (Fries, *Annalen*, 1912, **389**, 305), and 3-chloro-2 : 4 : 6-trinitrophenol. Auwers and Deines (*Zentr.*, 1924, II, No. 18) have prepared 6- and 4-nitro-3-chlorophenols *via* the action of nitrous acid on 3-chloroaniline nitrate, but we have obtained very moderate yields by their method.

The present paper relating to the nitro-derivatives obtainable from *m*-chlorophenol by direct nitration is part of a systematic study of the chemistry of *m*-halogenated phenols.

The above mononitro-compounds have been prepared in purer form than any hitherto described and 3-*chloro*-2-*nitrophenol* has been obtained in excellent yield. 4 : 6-, 2 : 6-, and 2 : 4-Dinitro-3-chlorophenols are readily distinguishable by means of their characteristic silver salts.

Monosulphonation of *m*-chlorophenol at 100—120° appears to form exclusively 3-chlorophenol-4-sulphonic acid, owing to the usual directing influence of the hydroxyl group.

3-Chloro-2 : 4 : 6-trinitrophenol is obtained in a very pure con-

dition by the direct nitration of *m*-chlorophenol and removal of any dinitro-compound in steam. If, however, *m*-chlorophenol is sulphonated and then treated with an excess of nitric acid, a trinitro-sulphonic acid is formed which on hydrolysis yields 3-chloro-2 : 5 : 6-trinitrophenol as a product volatile in steam.

Evidence in support of the constitution assigned to 3-chloro-4-nitrosophenol by Hodgson and Moore (J., 1923, **123**, 2499) has been obtained by its oxidation to 3-chloro-4-nitrophenol.

Experimental.

Mononitration of m-*Chlorophenol.*

6- *and* 4-*Nitro*-3-*chlorophenols.*—*m*-Chlorophenol (24 g.), liquefied by alcohol (2 c.c.), was added slowly to a solution, kept below 25°, of 40 g. of concentrated sulphuric acid and 29 g. of sodium nitrate in 70 c.c. of water. After being stirred for 2 hours, the mixture was diluted with water (2 vols.). The solid was washed and steam-distilled. The yellow oil in the distillate solidified and after being pressed was again distilled in steam, when 3-chloro-6-nitrophenol, m. p. 41°, was obtained (Auwers and Deines, *loc. cit.*, give 39°) (Found : Cl, 20·4. Calc., Cl, 20·5%). The yield of crude product was 22%.

3-Chloro-4-nitrophenol, which remained in the distillation flask as a brown solid, m. p. 80—106° (yield 60%), crystallised in white, feathery needles, m. p. 121—122°, from dilute hydrochloric acid or water (Found : Cl, 20·4%). Auwers and Deines (*loc. cit.*) obtained faintly yellow needles, m. p. 120—121°, from benzene; the colour was possibly due to the action of atmospheric ammonia. We cannot confirm Uhlemann's statement (*loc. cit.*) that 3-chloro-6-nitrophenol melts at a second determination at 32° and regains its normal m. p. after several days.

Oxidation of 3-*Chloro*-4-*nitrosophenol.*—A solution of the nitrosophenol (2 g.) in 400 c.c. of water containing 20 g. of sodium hydroxide and 20 g. of potassium ferricyanide was acidified with sulphuric acid after being kept for 2 days. Ether extracted from the mixture a trace of a product which was volatile in steam and gave a red sodium salt, but the bulk of the extract was 3-chloro-4-nitrophenol, which melted at 121° after crystallisation from water (Found : Cl, 20·3%).

Oxidation with nitric acid of various strengths and with hydrogen peroxide produced similar results, but the yields were unsatisfactory.

3-*Chloro*-2-*nitrophenol.*—*m*-Chlorophenol (12·8 g.) was added slowly to 75 g. of oleum (27% SO_3), cooled after each addition.

The mixture was kept for 12 hours and then heated for 2 hours on a water-bath to complete the disulphonation. Nitric acid (4·5 c.c.; *d* 1·5) dissolved in 20 c.c. of oleum (27% SO_3) was added during 15 minutes to the cooled mixture, which was then kept for 2 hours. On dilution and hydrolysis in a current of steam, a viscous, yellow, opaque oil passed over which rapidly solidified; it separated in white, slender needles, m. p. 37·5°, from its yellow solution in light petroleum (yield 11 g.; 66%) (Found: Cl, 20·35. $C_6H_4O_3NCl$ requires Cl, 20·5%).

3-Chloro-2-nitrophenol is remarkable as being an *o*-nitrophenol which is colourless. It is readily turned yellow by atmospheric ammonia. Like its 6-nitro-isomeride, it has a distinctive odour; the 4-nitro-isomeride is odourless. The *silver* salt of 3-chloro-2-nitrophenol forms characteristic crimson festoons (Found: Ag, 38·2. $C_6H_3O_3NClAg$ requires Ag, 38·5%). The *methyl* ether was prepared by means of boiling aqueous sodium carbonate and excess of methyl sulphate. The product was steam-distilled and the white solid crystallised from dilute alcohol; m. p. 55° (Found: Cl, 18·7. $C_7H_6O_3NCl$ requires Cl, 18·9%). The *benzoate* could not be prepared in aqueous alkali hydroxide, but was readily obtained in aqueous sodium carbonate. It separated from alcohol in colourless crystals, m. p. 123° (Found: Cl, 12·1. $C_{13}H_8O_4NCl$ requires Cl, 12·7%).

Dinitration of m-*Chlorophenols.*

General Procedure.—The initial material is added gradually to a cooled mixed acid containing 98% sulphuric acid (15 vols.), 70% nitric acid (12 vols.), and water (9 vols.). After an interval, the mixture is warmed if necessary, diluted, and steam-distilled. The dinitro-products are all volatile with steam and crystallise well from water or dilute acids.

3-*Chloro*-4 : 6-*dinitrophenol.*—(*a*) The reaction mixture (1 g. of 3-chloro-6-nitrophenol and 3 c.c. of mixed acid; 3 c.c. of concentrated sulphuric acid were subsequently added) was kept for 2 hours and then heated for ½ hour on the water-bath. 3-Chloro-4 : 6-dinitrophenol was obtained in colourless crystals, m. p. 92—93°, from water or in stout prisms from light petroleum (Found: Cl, 16·1. Calc., Cl, 16·2%). A non-volatile product was 3-chloro-2 : 4 : 6-trinitrophenol, large, white needles, m. p. 114° (from water).

(*b*) The reaction mixture (1 g. of 3-chloro-4-nitrophenol and 4 c.c. of mixed acid) was kept over the week-end. The product had m. p. 92—93° (Found: Cl, 16·15%).

(*c*) 1 : 3-Dichloro-4 : 6-dinitrobenzene was boiled with aqueous sodium carbonate, and the solution acidified after filtration. The precipitate melted at 92° after being crystallised from water.

The identity of the three products in (*a*), (*b*), and (*c*) was established by the melting points of their mixtures.

3-*Chloro*-2 : 6-*dinitrophenol*.—(*a*) This was obtained from a reaction mixture of 2 g. of 3-chloro-2-nitrophenol and 12 c.c. of mixed acid. It is less volatile with steam than its 4 : 6-dinitro-isomeride and crystallises from dilute hydrochloric acid in white, feathery crystals, m. p. 114·5° (Found : Cl, 16·1. Calc., Cl, 16·2%). A non-volatile product was 3-chloro-2 : 4 : 6-trinitrophenol (Found : Cl, 13·2. Calc., Cl, 13·5%).

(*b*) A mixture of 4 g. of 3-chloro-2-nitrophenol and 4 c.c. of oleum (27% SO_3) was kept over-night (crystals of unchanged material separated), 4 c.c. of oleum were added and, 4 hours later, the mixture was heated on the water-bath to complete the sulphonation. It was then nitrated with 1 c.c. of nitric acid (*d* 1·5) dissolved in 2·5 c.c. of oleum. The product volatile with steam was 3-chloro-2 : 6-dinitrophenol. The liquor in the flask, on neutralisation with potassium carbonate, gave a bright yellow potassium salt (probably of 3-chloro-2 : 6-dinitrophenol-4-sulphonic acid) from which 3-chloro-2 : 6-dinitrophenol was obtained on hydrolysis.

(*c*) A mixture of 3 g. of *m*-chlorophenol and 7 c.c. of oleum (27% SO_3), after being kept for 2 hours, was nitrated with 0·8 c.c. of nitric acid (*d* 1·5) in 4 c.c. of oleum and kept for 1 hour. The volatile product of hydrolysis by steam was 3-chloro-2 : 6-dinitrophenol (mixed m. p.).

3-*Chloro*-2 : 4-*dinitrophenol*.—After 3 g. of 3-chloro-2-nitrophenol had been added slowly to 1·8 c.c. of sulphuric acid (100%) and 4 c.c. of oleum (27% SO_3), the mixture was kept for 6 hours, then heated on the water-bath for 2 hours, cooled, nitrated with 0·8 c.c. of nitric acid (*d* 1·5) in 4 c.c. of oleum, and kept for 1 hour. The steam-distillate, on cooling, deposited 3-chloro-2 : 6-dinitrophenol. The filtrate from this, on extraction with ether, gave up a solid, probably 3-chloro-2 : 4-dinitrophenol, which, after repeated fractional crystallisation from water, had m. p. 138—140° and gave a yellow silver salt insoluble in ammonia (Found : Cl, 15·9. Calc., Cl, 16·2%).

Direct Nitration of Disulphonated m-*Chlorophenol*.—After remaining for 20 hours at 10—15°, a solution of 4·2 g. of *m*-chlorophenol in 25 g. of oleum (27% SO_3) was nitrated with 2·7 c.c. of nitric acid (*d* 1·5) in 14 c.c. of oleum and kept for 1 hour. On hydrolysis in a current of steam, 3-chloro-2-nitrophenol distilled over first and was followed by 3-chloro-2 : 6-dinitrophenol, which separated, and 3-chloro-2 : 4-dinitrophenol, which was extracted with ether, from the distillate. The presence of 3-chloro-4 : 6-dinitrophenol was not detected.

Sulphonation and Nitration of 3-*Chloro*-4-*nitrophenol.*—A solution of 5 g. of the chloronitrophenol in 10 c.c. of oleum (27% SO_3) was cooled and immediately nitrated with 1·2 c.c. of nitric acid (*d* 1·5) in 5 c.c. of oleum. After the usual treatment 3-chloro-4 : 6-dinitrophenol, but not 3-chloro-2 : 4-dinitrophenol, was obtained. If, however, the sulphonation mixture was kept for 2 hours, or was warmed, before being nitrated, no 3-chloro-4 : 6-dinitrophenol was produced, the destruction of 3-chloro-4-nitrophenol by oleum being thus made manifest. 2- and 6-Nitro-3-chlorophenol are stable towards oleum.

Properties of the Dinitro-m-*chlorophenols.*—4 : 6-, 2 : 6-, and 2 : 4-Dinitro-3-chlorophenol are in the order of increasing solubility in water. The solutions are yellow. The silver salts are prepared from the ammonium salts and silver nitrate in neutral aqueous solution. The 4 : 6-dinitro-compound gives a characteristic yellow gel which slowly becomes crystalline (Found : Ag, 33·0. Calc., Ag, 33·2%). The 2 : 4-dinitro-compound forms yellow crystals (Found : Ag, 32·95%). The 2 : 6-dinitro-compound gives a red, crystalline substance which is much more soluble in aqueous ammonia or water than either of the other two (Found : Ag, 32·9%). The silver salts of 2 : 6-dinitrophenol and 4-chloro-2 : 6-dinitrophenol also are red.

The three dinitro-*m*-chlorophenols resist methylation and benzoylation by direct means. The mononitro-compounds are methylated only with difficulty.

Trinitration of m-*Chlorophenol.*

3-*Chloro*-2 : 4 : 6-*trinitrophenol.*—*m*-Chlorophenol (4 g.) dissolved in 6 c.c. of oleum (27% SO_3) was nitrated in the cold with 40 c.c. of nitric acid (70%), added gradually. The mixture, having been stirred for 1 hour, was gently boiled for 10 minutes and poured on to ice, and products volatile with steam (if any) were removed. The residue crystallised from dilute sulphuric acid in fern-like crystals and from water in rectangular prisms, m. p. 114° (Found : Cl, 13·2. Calc., Cl, 13·5%).

3-Chloro-2 : 4 : 6-trinitrophenol is readily soluble in alcohol, ether, benzene, or chloroform. Its sodium and silver salts are yellow; the former is moderately soluble in water, and the latter insoluble in aqueous ammonia. It is the ultimate product of nitration of all the mono- and di-nitro-3-chlorophenols mentioned above.

3-*Chloro*-2 : 5 : 6-*trinitrophenol.*—*m*-Chlorophenol (5 g.) dissolved in concentrated sulphuric acid (3 c.c.) was heated for 9 hours at 120°, cooled, and poured into 50 c.c. of water. The solution was

filtered from tar, treated with 15 c.c. of nitric acid (*d* 1·5), and, after being stirred for 30 minutes, was slowly heated and finally boiled for 5 minutes. Neutralisation of the cooled filtered solution with solid potassium carbonate caused the precipitation of a yellow product, which crystallised from water in characteristic old-gold clusters and from alcohol, in which it was moderately soluble, in small, yellow needles [Found : S, 7·5; Cl, 8·0. Calc. for $C_6Cl(OK)(NO_2)_3 \cdot SO_3K$, S, 7·6; Cl, 8·5%]. This salt was hydrolysed with boiling dilute sulphuric acid in a current of steam, and the volatile product, m. p. 112·5—113·5°, being somewhat soluble in water, was extracted from the distillate with ether (yield 2·7 g.) (Found : Cl, 13·2; N, 16·5. $C_6H_2O_7N_3Cl$ requires Cl, 13·5; N, 15·9%). The yellow, crystalline silver salt is insoluble in aqueous ammonia.

This steam-volatile trinitro-compound, produced from a monosulphonic acid in which the sulpho-group appears to be in position 4, is probably 3-chloro-2 : 5 : 6-trinitrophenol.

Traces of 4 : 6- and 2 : 4-dinitro-3-chlorophenol were detected when the original nitration mixture was steam-distilled without previous neutralisation.

The authors thank the British Dyestuffs Corporation for gifts of chemicals in connexion with this investigation.

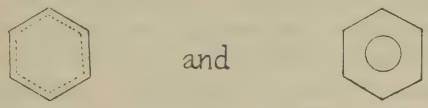
TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, December 17th,* 1924.]

CCXI.—*Polynuclear Heterocyclic Aromatic Types. Part II. Some Anhydronium Bases.*

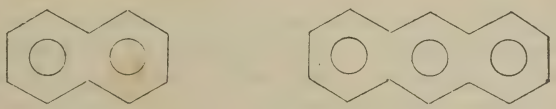
By JAMES WILSON ARMIT and ROBERT ROBINSON.

IT is a commonplace of the electronic theory of the atom and of valency that certain systems of electrons exist which by their association reach a stable condition, and an example may be found in the electron pair or duplet, the octet and dodecet, as well as in the special configurations, which are frequently assumed, of the valency electrons in nitrogen, carbon monoxide, and similar substances. The occurrence of many atoms in a molecule provides further opportunities for the emergence of electron groups of marked stability and, *ceteris paribus*, the possession of such groups confers chemical stability as shown, for example, by reduced unsaturation and a tendency to maintain the type. These are, of course, the chief characteristics of benzenoid systems, and here the explanation is obviously that six electrons are able to form a group which

resists disruption, and may be called the *aromatic sextet.** It is not supposed that the existence of the sextet involves a change in the total covalency exerted by the carbon atoms of the ring nor does the theory as employed below require any particular assumption in regard to the position of the electrons or their orbits in space. Thus the symbols



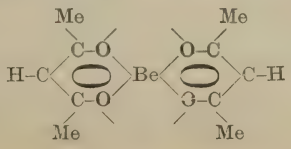
are each considered to express a view of one aspect of the problem and are not inconsistent. The first expression suggests a symmetrical distribution of electrons in the ring, and in regard to the covalencies should be taken as the interpretation of the second expression. The circle in the ring symbolises the view that six electrons in the benzene molecule produce a stable association which is responsible for the *aromatic* character of the substance.† Naphthalene and anthracene will be represented by the following formulæ



in which the deletion of the central connecting bonds is more apparent than real, because these attachments are by covalencies which involve the electrons of the sextets only. The aromatic character of thiophen and pyrrole requires the hetero-element to have contributed some of its free salt-forming electrons for the purpose of setting up a sextet, with the natural result that the basic character of these substances has been suppressed or largely diminished. In pyridine, the sextet can, however, be obtained without the help of the *lone pair* on the nitrogen atom. The

* In the ions of carboxylic acids, in the *cyclo*pentadienes and indene derivatives, and in many other types of *semi-aromatic* compounds, groups of two or four electrons may be assumed to occur.

† The stability of beryllium acetylacetone and similar substances may be associated with the fact that the rings are aromatic and contain sextets. This is possible if the function of all the oxygen atoms is assumed to be identical as in the annexed formula.

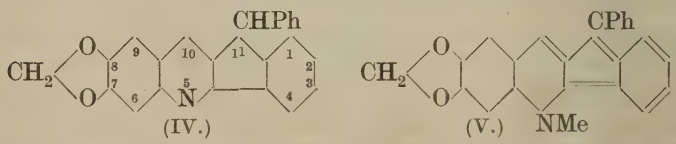


formulæ with sextets do not necessarily represent systems the aromatic character of which is of the most perfected kind. There is ample evidence that in some typical aromatic compounds the valency is unevenly distributed, and consideration of such a series as pyridine, benzene, naphthalene, anthracene, glyoxaline, thiophen, pyrrole, and furan serves to protect us from the unwarranted assumption that there are no gradations between the Kekulé formula and the symmetrical electronic structures which have been proposed for benzene. In discussing the possibility of the existence of the pentamethine nucleus in fusion with other rings, we pointed out (J., 1922, **121**, 828) that, on the basis of the cyclic conjugation theory, the forms I, II, and III might occur.



(I.) (II.) (III.)

On applying the restriction on the cyclic conjugation theory which is now suggested, namely, that the number of electrons must be such that sextets can be formed in each ring, it is clear that II and III cannot satisfy the condition.* The type represented by I remains theoretically possible, and we have prepared a compound which appears to contain such a nucleus. 6-Aminopiperonal and 3-phenylindanone condensed in alcoholic solution with the aid of potassium hydroxide, producing the quinoline derivative (IV), the methosulphate of which yields, on decomposition with hot aqueous alcoholic potassium hydroxide, the anhydronium base (V).

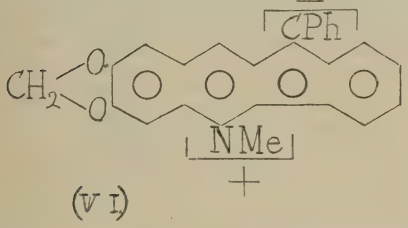


(IV.) (V.)

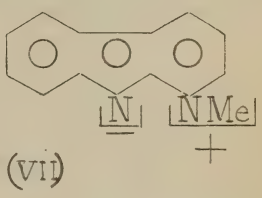
Utilising the free electrons on the nitrogen atom, 24 electrons are available for aromatic sextet formation as shown in (VI). Here the quadrivalent nitrogen is positively charged, whilst the pentamethine ring is negatively charged; (V) and (VI) represent extreme conditions, and the true structure doubtless lies between the two. (V) is not stable, because the right-hand benzene ring is

* The unsaturated nature of *cyclo*octatetraene suggests that a stable group of eight electrons analogous to the aromatic sextet is not formed.

not aromatic, and (VI) is not stable because it is a dipole; the tendencies to aromatic sextet formation and to neutralisation of the charges work in opposite directions and must reach some compromise. There is a very large class of substances which can similarly be regarded as normally occupying an intermediate position between a fully polarised aromatic phase and a neutralised quinonoid or ethenoid phase and these are usually anhydro-derivatives of aromatic *onium* hydroxides of various kinds. We propose to term these compounds *anhydronium bases*, since, although extremely diverse in form, they exhibit very similar chemical properties. Anhydronium bases derived from the methohydroxides of 4-carboline derivatives have been already described (Perkin and Robinson, J., 1919, **115**, 951; Kermack, Perkin, and Robinson, J., 1922, **121**, 1877; Robinson and Robinson, J., 1924, **125**, 832), whilst, in addition, 5-methyl-5-*iso*carboline has been recently prepared (Robinson and Thornley, J., 1924, **125**, 2169). We have now shown that 3-carboline methohydroxide loses water with the formation of an anhydride (VII). A corresponding substance in

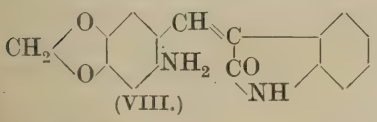


(VI)

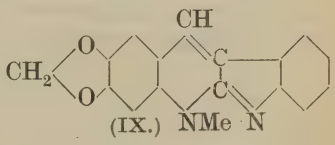


(VII)

the quinindoline series was obtained indirectly by condensation of 6-aminopiperonal with oxindole followed by treatment of the resulting aminopiperonylideneoxindole (VIII) with methyl sulphate and then with alcoholic potassium hydroxide, closing the ring with elimination of water.



(VIII.)

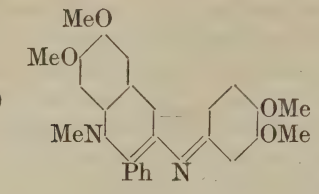


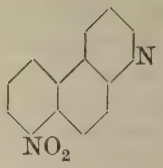
(IX.)

The base (IX) is represented in the quinonoid form, but it will be understood that we regard its actual mean condition as being something intermediate between this and the arrangement analogous to (VII). This remark applies to all formulæ here presented whether in the full polar aromatic conditions or as quinones. A bright scarlet anhydronium base in the 4-carboline series (harmine type) has been prepared by the decomposition of phenyldiveratro-

harmyrine methosulphate with sodium hydroxide and has the constitution (X).

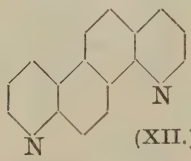
(X.)



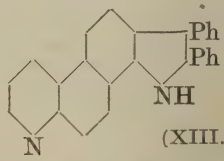


(XI.)

Anhydronium bases of what is fundamentally the glyoxaline or pyrazole type can therefore be obtained in the 3-, 4-, or 5-carboline series, the two nitrogen atoms in different rings being separated by one, two, or three carbon atoms. It was of interest to find out whether much greater separation is possible and experiments were undertaken with this object. The nitration of β-naphthaquinoline was studied by Claus and Besseler (*J. pr. Chem.*, 1898, **57**, 49), but the constitution of the mononitro-derivative was not determined. We have oriented the substance (XI) by the observation that the related aminonaphthaquinoline is converted by an application of the Skraup reaction into a naphthadiquinoline (XII), which may also be obtained from 1 : 6-naphthylenediamine in a similar manner.

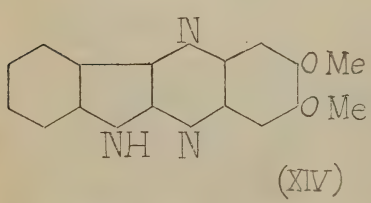


(XII.)

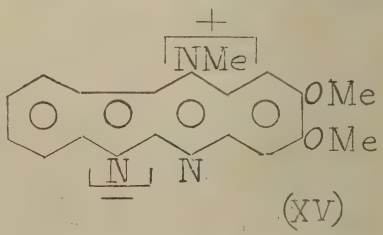


(XIII.)

Amino-β-naphthaquinoline was changed to an indole derivative (XIII) by condensation with benzoin under conditions similar to those used by Japp and Murray (J., 1894, **65**, 889) in analogous cases. The results obtained on decomposing the methosulphate of (XIII) were ambiguous and indicated oxidation. We have also investigated the alkylation of an indophenazine derivative (XIV). In view of such facts as the weak basic character of the amidines



(XIV)

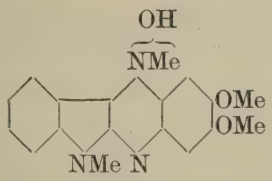


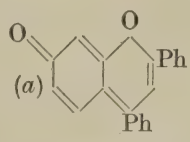
(XV)

and the circumstance that *p*-phenylenediamine is a stronger base than the *m*-isomeride, it seems most probable that the first methyl

group will attach itself to the quinoxaline nitrogen which is the more remote from the nitrogen of the indole nucleus, but there is no direct proof of this. On such an assumption, the anhydronium base derived from the methohydroxide of (XIV) will have the constitution (XV). This orange-red substance can be converted into a remarkably stable methohydroxide (XVI).

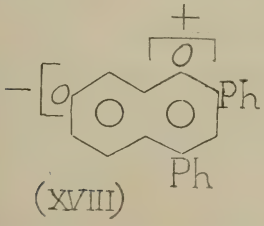
(XVI.)



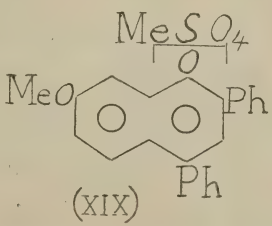


(XVII.)

It has already been stated that the anhydronium bases include many types and among these are the glyoxalines, pyrazoles, α- and γ-aminopyridines, α- and γ-pyridones, α- and γ-pyrones, carbolines and *iso*carbolines, diazo-oxides and diazoimines * derived from *o*- and *p*-hydroxy- and amino-diazonium hydroxides, fuchsones and fuchsonimines, quinopyridanes, pyranhydrones, derivatives of methylenexanthane, etc. Thus the anhydropyranol (XVII) can also be represented as a phenol-betaine (XVIII), and it is the anhydr-



(XVIII)



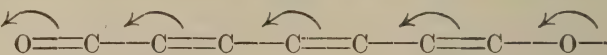
(XIX)

onium base derived from hydroxydiphenylbenzopyrylium hydroxide. As such, it shows the normal behaviour of its type and adds on methyl sulphate so as to form the pyrylium salt (XIX) by direct addition of a methyl group to the quasiquinonoid oxygen atom.

Finally, it is necessary to indicate an important consideration. The formation of an anhydronium base invariably involves a redistribution of the charge unless the positive and negative centres in the dipole are so powerfully basic and acidic that the substance is definitely a betaine. It is convenient to keep the latter separate and to reserve the expression *anhydronium base* for the compounds which are recognisably intermediate between neutral and fully polarised forms. The redistribution of charge referred to can only

* On this hypothesis, the action of methyl iodide on a diazo-oxide or diazoimine should result in the replacement of the diazo-group by iodine and the simultaneous attachment of methyl to oxygen or nitrogen, respectively.

take place if the system connecting the charged centres is a conducting system. In other words, the necessary changes in covalency must be, not merely possible, but facile, and this will be the case only with definitely conjugated systems. There must always be a possible mechanism for the transfer of the charge in accordance with the electronic theory of conjugation as in the scheme:



and this will be the case if the formula of the substance can be constructed on the classical valency theory with alternate single and double bonds. For example, if the oxygen in (XVII) is at (*a*), the condition cannot be satisfied, and therefore 6-hydroxy-2 : 4-diphenylbenzopyrylium hydroxide should not yield an anhydronium base, although it might give a betaine on the model of (XVIII). The conception of the electrical conductivity of conjugated systems is implicit in all the suggestions relating to the mechanism of addition to such systems made by Kermack and Robinson (J., 1922, **121**, 427), and for experimental evidence we can turn to graphite, each one of the layers of which must be regarded as comprising a single fully conjugated aromatic system.

Experimental.

7 : 8 - *Methylenedioxy* - 11 - *phenylindenoquinoline* (IV).—Aqueous potassium hydroxide (5 c.c of 50%) was added to a cold solution of 6-aminopiperonal (3·9 g.) and 3-phenylindanone (5·1 g.) in ethyl alcohol (45 c.c.), when the liquid darkened and a red, crystalline precipitate slowly formed. Next day the separation had become copious and the substance was collected, washed with alcohol, and dried at 100° (6·6 g.). The compound crystallises from benzene in hexagonal prisms or in microscopic needles if the solution is rapidly cooled; it has m. p. 245—246° (Found: C, 81·6; H, 4·8; N, 4·3. $C_{23}H_{15}O_2N$ requires C, 81·9; H, 4·5; N, 4·2%). The base is moderately readily soluble in hot benzene or chloroform, very sparingly soluble in hot alcohol, and almost insoluble in ether or light petroleum. The red solution in sulphuric acid exhibits intense violet fluorescence, changing to blue fluorescence on dilution with water. Unlike the related methylenedioxyindenoquinoline (Part I, p. 831), this phenyl derivative is precipitated by the addition of water to its solution in glacial acetic acid. The *hydrochloride*, decomp. 247°, and the *picrate*, decomp. 236°, crystallise in yellow needles. The *methosulphate* separated in the course of 30 minutes from a boiling solution of the base (3 g.) and methyl sulphate (27 c.c.) in benzene (130 c.c.). The precipitate (3·8 g.) crystallised

from ethyl alcohol in pale yellow needles, m. p. 233° (Found : S, 7·0. $C_{25}H_{21}O_6NS$ requires S, 6·9%). The salt is moderately readily soluble in hot water and its aqueous and alcoholic solutions exhibit intense bluish-violet fluorescence. The *methiodide*, obtained directly or by double decomposition of the methosulphate, is sparingly soluble in water and alcohol and crystallises from the latter in small, pale yellow needles, m. p. 241—242° (decomp.).

Anhydro-7 : 8-*methylenedioxy*-11-*phenylindenoquinoline Methohydroxide* (V, VI).—On addition of aqueous potassium hydroxide (5 c.c. of 50%) to a hot solution of the preceding methosulphate (1 g.) in aqueous alcohol (80 c.c. of 50%), there was an immediate separation of pale green, very slender, microscopic needles. The mixture was boiled for 1 minute, filtered hot, and the residue well washed with hot alcohol and dried in a vacuum at 100° until its weight was constant (0·65 g.) (Found : C, 81·4; H, 5·0; N, 4·2. $C_{24}H_{17}O_2N$ requires C, 82·0; H, 4·8; N, 4·0%). The substance is readily soluble in chloroform to an emerald-green solution, and by careful addition of light petroleum it can be precipitated in small, green needles which darken at 226°, progressively decompose at higher temperatures, and finally melt to a black liquid at 246—247°. It is less readily soluble in benzene or toluene and undergoes decomposition in these media, which change is, however, no doubt due to oxidation. The base is slightly soluble in boiling water, the solution exhibiting bright blue fluorescence, and with acids the methosalts of the parent base are regenerated. The *picrate* crystallises in pale yellow needles which sinter at 221° and melt at 226°. The readily soluble *methiodide* of this anhydro-base is a pale yellow substance which gives an orange, amorphous precipitate with potassium hydroxide in aqueous solution. The new compound is easily soluble in cold water to a yellow fluorescent solution and is clearly a methohydroxide. It shows no tendency to give an anhydro-base and behaves exactly as would be anticipated if the methylation had proceeded so as to produce the group $-CMePh-$. A quite similar case was described in Part I (p. 834), and we are of the opinion that the analogy supports our view of the nature of the substance which is now under discussion. The green colour of the base may, however, be due to impurity.

3-*Methyl*-3-iso*carboline* (VII).—3-Carboline (Lawson, Perkin, and Robinson, J., 1924, **125**, 626), prepared by the improved method of Robinson and Thornley (*ibid.*, p. 2169), readily yields a *methosulphate* when its solution in hot nitrobenzene is treated with a solution of neutral methyl sulphate in toluene. The derivative is readily soluble in water and but sparingly soluble in alcohol, from which it crystallises in stellate clusters of pointed needles.

A concentrated aqueous solution was decomposed by an excess of warm 40% potassium hydroxide, and the base at once extracted by a large volume of light petroleum. The solution was dried with powdered potassium hydroxide and then with anhydrous barium oxide, filtered, and distilled with every precaution to avoid access of moist air. At a certain stage, crystallisation of the anhydro-base commenced and after cooling the small, yellow prisms, m. p. 140°, were collected (Found : in material dried at 95° in a high vacuum, C, 78·8; H, 5·6. $C_{12}H_{10}N_2$ requires C, 79·1; H, 5·5%).

The base is soluble in water, the solution being colourless and having an alkaline reaction. Aqueous acid solutions do not exhibit fluorescence. The base combines with methyl iodide to form a nearly colourless salt, which with silver oxide gives an alkaline, faintly fluorescent solution. The methohydroxide so obtained is precipitated by the addition of sodium hydroxide and exhibits no tendency to give an anhydro-base.

6′-Aminopiperonylideneoxindole (VIII).—Aqueous potassium hydroxide (8 c.c. of 60%) was added to a cold solution of oxindole (3 g.) and 6-aminopiperonal (3·2 g.) in methyl alcohol (40 c.c.). The precipitate of fine, orange needles which formed when the darkened liquid was stirred was washed with methyl alcohol, dried at 100°, and twice crystallised from ethyl alcohol to remove persistent inorganic contamination. The deep orange needles (3·1 g.) obtained decomposed at 226° (Found : C, 68·3; H, 4·7. $C_{16}H_{12}O_3N_2$ requires C, 68·6; H, 4·3%). The base is to some extent soluble in boiling water to an orange solution, it is freely soluble in acetic acid or nitrobenzene and sparingly soluble in benzene. The mineral acid salts are sparingly soluble, pale yellow, crystalline substances. The *picrate* crystallises from ethyl alcohol in deep yellow needles, which darken at 235° but do not melt at 300°. The orange solution in sulphuric acid is not fluorescent, but if the salts of the base are decomposed by alkali and the product is dissolved in sulphuric acid, the solution exhibits intense bluish-violet fluorescence, which is clearly due to the formation of methylenedioxyquinindoline. The diazo-solution from the base is pale yellow and gives a crimson coloration with alkaline β-naphthol. The *methosulphate* (*6′-methylamino-piperonylideneoxindole methyl hydrogen sulphate*) was obtained in the following manner. The base (1·5 g.) was dissolved in nitrobenzene (30 c.c.) and toluene (30 c.c.), a solution of neutral methyl sulphate in toluene (10 c.c. of 75%) added to the boiling mixture, and the lamp removed. The derivative, which separated in a few minutes as a flocculent precipitate of yellow needles, was crystallised from 50% alcohol, washed with ether, and dried at 120° (1·2 g.) (Found : S, 7·8. $C_{18}H_{18}O_7N_2S$ requires S, 7·9%). The salt darkens at 289°,

but does not melt at 300°. It is sparingly soluble in water or ethyl alcohol, but more readily soluble in a mixture of the two. The open-chain structure is indicated chiefly by the fact that the solution in sulphuric acid is not at once fluorescent, but on standing for a few minutes acquires a phenomenal bluish-violet fluorescence.

10 : 11-*Anhydro*-7 : 8-*methylenedioxyquinindoline* 10-*Methohydroxide* (IX).—The pale lemon-yellow needles that formed almost immediately when aqueous potassium hydroxide (10 c.c. of 60%) was added to the preceding methosulphate (1 g.) dissolved in boiling aqueous alcohol (80 c.c. of 50%) were crystallised from alcohol, in which they were moderately readily soluble, and dried in a vacuum at 120° (0·5 g.), the substance becoming deep orange whilst seeming to retain the crystalline structure (Found : C, 74·0; H, 4·5; N, 10·3. $C_{17}H_{12}O_2N_2$ requires C, 73·9; H, 4·4; N, 10·2%). This base, m. p. 244°, is relatively stable and can be sublimed when carefully heated. It dissolves in sulphuric acid, the solution exhibiting a beautiful bluish-violet fluorescence. The mineral acid salts and the picrate crystallise in yellow needles. On boiling with water, reversion to the methohydroxide of the quinindoline derivative was observed.

Py-N-*Methylphenyldiveratro*iso*harmyrine* (X).—A solution of phenyldiveratroharmyrine (3 g.) (Lawson, Perkin, and Robinson, *loc. cit.*) in benzene (100 c.c.) was boiled with neutral methyl sulphate (3 g.) for 5 minutes, and the orange-yellow, crystalline product was washed with benzene, crystallised from ethyl alcohol (in yellow needles), and dried at 120° (Found : C, 59·9; H, 5·2. $C_{27}H_{28}O_8N_2S$ requires C, 60·0; H, 5·2%). In alcoholic solution, this salt exhibits bright green fluorescence. Its yellow, aqueous solution was decomposed with sodium hydroxide, the scarlet precipitate washed with aqueous sodium hydroxide, dried in a vacuum, and dissolved in a considerable volume of hot benzene. This solution was dried with potassium hydroxide, and most of the solvent distilled, when the new base crystallised in bright scarlet, dense clusters of prismatic needles which darken above 140°, are chocolate at 240°, black at 260°, and melt at 264° with further decomposition (Found : in material dried at 110° in a high vacuum; C, 72·7; H, 5·7; N, 6·4. $C_{26}H_{24}O_4N_2$ requires C, 72·9; H, 5·6; N, 6·5%). The solution in neutral solvents such as ether or benzene has a fine violet fluorescence, but in alcohol or water the base gives a yellow solution with green fluorescence and has obviously reverted to phenyldiveratroharmyrine methohydroxide. Its yellow solution in sulphuric acid exhibits intense yellowish-green fluorescence and becomes deep ivy-green on heating. The base forms a *methiodide* which is sparingly soluble in ethyl alcohol and crystallises in slender, short, microscopic,

yellow needles, m. p. 266—267°. This salt exhibits green fluorescence in solution and gives no precipitate with ammonia or sodium carbonate in aqueous solution (solutions of the anhydro-base are so precipitated), whilst with sodium hydroxide in excess it gives a pale yellow precipitate of a stable methohydroxide, soluble in water.

(1 : 6)-*Naphthadiquinoline* (XII).—β-Naphthaquinoline was nitrated according to Claus and Besseler (*loc. cit.*), and the nitro-derivative reduced in the following manner : A solution of crystallised sodium sulphide (45 g.) in water (50 c.c.) was gradually added to a boiling solution of nitro-β-naphthaquinoline (16 g.) in aniline (100 c.c.), causing a vigorous reaction. The liquid was boiled for 30 minutes, the aniline distilled in steam, and the residue crystallised from 30% aqueous alcohol, 8 g. of amino-β-naphthaquinoline, m. p. 158°, being obtained. The diquinoline was obtained by the methods (A) and (B). (A) A mixture of amino-β-naphthaquinoline (13 g.), nitrobenzene (7·5 g.), sulphuric acid (20 g.) and glycerol (25 g.) was heated (oil-bath at 150—160°) during 6 hours. The base was rendered to ether (6 extractions), and the solution dried and concentrated to small bulk, when pale yellow needles (2·1 g.) slowly separated. The substance is sparingly soluble in ether, benzene, or alcohol (Found : C, 83·3; H, 4·6; N, 12·5. $C_{16}H_{10}N_2$ requires C, 83·5; H, 4·4; N, 12·2%).

(B) 5-Nitro-2-naphthylamine (3·4 g.) was gradually added to 60% acetic acid (60 c.c.) and iron filings (10 g.) at the temperature of the steam-bath. When the red colour had disappeared, water (100 c.c.) was added, and the solution was boiled for 5 minutes and filtered into dilute sulphuric acid (150 c.c. of 25%); the colourless needles of 1 : 6-naphthylenediamine sulphate obtained on cooling were dried (6·1 g.). A mixture of this sulphate (6 g.), nitrobenzene (4 g.), glycerol (16 g.), and sulphuric acid (16 g.) was heated (oil-bath at 155—165°) for 4·5 hours. The diquinoline was extracted from the solution, diluted and made strongly alkaline, by means of ether and 0·6 g. was ultimately obtained in colourless needles, by crystallisation from acetone. The substances prepared by methods (A) and (B) or a mixture of the two melted at 183·5—184·5°. Both specimens dissolve in dilute sulphuric acid, the colourless solutions exhibiting a bright blue fluorescence. The *sulphate* prepared from either of the specimens darkens above 250° and melts indistinctly at 268°.

5 : 6-(2 : 3-*Diphenylindolo*) (6 : 7)-*quinoline* (XIII).—An intimate mixture of amino-β-naphthaquinoline (7 g.), its dihydrochloride (3 g.), and benzoin (20 g.) was heated at 180—190° for 4 hours. The product was extracted by boiling benzene (150 c.c.) for 10 minutes, and the reddish-brown residue was separated from the hot

solution and triturated with aqueous potassium hydroxide. The isolated, washed, and dried product crystallised from nitrobenzene (50 c.c.) in colourless platelets (4 g.), which began to decompose at 298° (Found : C, 88·0; H, 5·0; N, 7·9. $C_{27}H_{18}N_2$ requires C, 87·6; H, 4·9; N, 7·6%). This base is very sparingly soluble in most organic solvents and forms very sparingly soluble, yellow salts with mineral acids. The solution in sulphuric acid exhibits green fluorescence which is persistent on dilution with water. When a trace of sodium nitrite or potassium dichromate is added to the sulphuric acid solution, an intense emerald-green coloration is developed. The *acetate* crystallises from glacial acetic acid in yellow needles decomposing above 300° (Found : C, 77·5; H, 5·4. $C_{27}H_{18}N_2,C_2H_4O_2,H_2O$ requires C, 77·7; H, 5·4%). A 75% solution (20 c.c.) of methyl sulphate in toluene was added to a boiling solution of the base (2 g.) in nitrobenzene (60 c.c.), the source of heat removed, the mixture cooled, ether added (200 c.c.), and the product (2·6 g.) crystallised from boiling alcohol, the *methosulphate* being obtained in intense yellow needles which become scarlet at about 165°; it is almost insoluble in boiling water (Found : S, 6·3. $C_{29}H_{24}O_4N_2S$ requires S, 6·5%). The decomposition of this methosulphate by alcoholic potassium hydroxide gave a crimson precipitate of microscopic needles, m. p. 225° (decomp.) if quickly heated, but we were unable to reach a definite conclusion in regard to the nature of the substance. It is reconverted by mineral acids into yellow, crystalline salts.

2 : 3-*Dimethoxyindophenazine* (XIV).—This substance was readily obtained by a slight modification of the method employed by Schunck and Marchlewski in the preparation of indophenazine (*Ber.*, 1895, **28**, 2528). 4 : 5-Dinitroveratrole (8 g.) was reduced in boiling acetic acid solution (200 c.c. of 50%) by the addition of zinc dust. When the colour changed from red to pale yellow, the solution was filtered and added to isatin (5 g.) dissolved in boiling acetic acid (125 c.c. of 20%). The yellow precipitate was collected after 5 minutes, washed with hot water, and dried at 150° (5·1 g.). The substance is readily soluble in hot nitrobenzene; it is sparingly soluble in boiling ethyl acetate or toluene, and separates from the latter in slender, yellow needles, m. p. 284° (Found : C, 68·8; H, 5·0; N, 15·1. $C_{16}H_{13}O_2N_3$ requires C, 68·8; H, 4·7; N, 15·0%). The neutral solutions have a violet-blue fluorescence and the cherry-red solution in sulphuric acid becomes deep purple on the addition of a trace of sodium nitrite or potassium dichromate. Mineral acid salts are bright yellow; the *hydrochloride*, m. p. 290° (decomp.), dissolves in water, the solution being yellow with green fluorescence, and in concentrated hydrochloric acid forming a blood-red solution.

The *picrate* crystallises from acetone in pale yellow needles, m. p. 254°. The *methosulphate* crystallised in large, flat, rectangular prisms on cooling a mixture obtained by the addition of a solution (100 c.c. of 75%) of methyl sulphate in toluene to a hot solution of the base (1·5 g.) in nitrobenzene (30 c.c.); a further quantity was precipitated by ether, the total yield being 2 g. The derivative crystallises from methyl alcohol in prisms, m. p. 247° (Found : S, 7·7. $C_{18}H_{19}O_6N_3S$ requires S, 7·9%). It is readily soluble in water, the solution exhibiting blue fluorescence, and is more sparingly soluble in alcohol.

2 : 3-*Dimethoxy*-5 (or 11)-*methyl*iso*indophenazine*(XV).—Potassium hydroxide (15 c.c. of 50%) was added to a boiling solution of the dimethoxyindophenazine methosulphate (2·7 g.) in 50% alcohol (60 c.c.). The deep red solution, on cooling, deposited voluminous, slender, scarlet needles which were washed with ether and dried at 120° (2·4 g.). The substance can be crystallised by careful addition of light petroleum to its benzene solution in scarlet needles sintering at 257° and melting at 261°, or from alcohol containing potassium hydroxide in scarlet prisms (Found : C, 69·3; H, 5·3; N, 14·4. $C_{17}H_{15}O_2N_3$ requires C, 69·6; H, 5·1; N, 14·3%). This base is moderately readily soluble in ethyl acetate or benzene, very readily soluble in chloroform, and sparingly soluble in ether. Like the parent dimethoxyindophenazine, it can be sublimed by careful heating in a tube. On boiling with water, an orange solution is obtained, and this becomes yellow after the addition of an acid. The *methiodide* crystallises in deep yellow needles, m. p. 205° (decomp.). If the dimethoxyindophenazine methosulphate is decomposed by potassium hydroxide in 50% alcohol in the cold, and the precipitate crystallised from the same solvent, slender, yellow needles, m. p. 278° (decomp.), of the *methohydroxide* are obtained (Found : C, 65·7; H, 5·2. $C_{17}H_{17}O_3N_3$ requires C, 65·6; H, 5·5·%). This substance is moderately readily soluble in hot water, forming a yellow solution. *Dimethoxymethyl*iso*indophenazine dimethosulphate* was obtained when a mixture of the anhydro-base (1·5 g.), methyl sulphate (10 c.c. of a 75% solution in benzene), and benzene (50 c.c.) was boiled until the red colour had completely disappeared. The precipitated yellowish-green, microscopic needles were washed with ether and dried at 100° (1·5 g.). The substance is very readily soluble in water and somewhat readily soluble in alcohol, from which it crystallises in orange needles, m. p. 238° (Found : S, 11·6. $C_{21}H_{27}O_{10}N_3S_2$ requires S, 11·7%). The solutions of the salt exhibit green fluorescence.

2 : 3-*Dimethoxy*-6-*methylindophenazine* 11 (or 5)-*Methohydroxide* (XVI).—Aqueous potassium hydroxide (10 c.c. of 50%) was added

to a hot solution of the preceding dimethosulphate (1 g.) in 50% alcohol (40 c.c.), when a momentary darkening occurred, giving place almost at once to an orange-yellow colour. The hot filtered solution soon deposited glistening, yellowish-orange needles (0·6 g.) and after recrystallisation from alcohol the substance melted at 164° (Found : C, 66·3; H, 6·0; N, 13·2. $C_{18}H_{19}O_3N_3$ requires C, 66·4; H, 5·9; N, 12·9%). The same substance was obtained by decomposition of dimethoxydimethylindophenazonium iodide. It is readily soluble in benzene, chloroform, alcohol, or acetone, sparingly soluble in alcohol or ether, and insoluble in light petroleum. The orange-yellow solution in dilute acids exhibits green fluorescence and the yellow solution in sulphuric acid becomes red when gently heated. Curious results followed on an attempt to introduce a third methyl group into the molecule. The base (0·5 g.), m. p. 164°, was heated in boiling benzene solution (16 c.c.) with methyl sulphate (4 c.c. of 75% solution in benzene) for 10 minutes. The dark brown oil which separated solidified on scratching and was collected and decomposed by aqueous-alcoholic potassium hydroxide. The product crystallised from aqueous alcohol in nearly colourless, silky needles, m. p. 85° (0·27 g.) (Found : C, 66·2; H, 6·2%). The compound appears to be different from the initial isomeride. It is much more soluble than the latter (m. p. 164°) and has a lower m. p. Possibly a methyl group has migrated to a new position, a suggestion which is clearly free from theoretical difficulty.

7-*Methoxy*-4-*phenylflavylium Salts* (XIX).—Anhydro-7-hydroxy-2 : 4-diphenylbenzopyranol (1 : 4) (1·5 g.), methyl sulphate (15 c.c. of a 75% solution in benzene), and benzene (50 c.c.), all of which had been carefully dried, were mixed and the liquid was boiled until the red colour had changed to orange-yellow. On cooling, pale yellow, glistening needles separated, and these were washed with ether and dried (1·2 g.) (Found : S, 7·4. $C_{23}H_{20}O_6S$ requires S, 7·5%). This *methosulphate*, m. p. 179°, is readily soluble in alcohol, acetic acid, acetone, or hot dilute hydrochloric acid, forming yellow solutions which exhibit very intense bluish-green fluorescence. The salt is to some extent hydrolysed by water. Addition of ether to the original mother-liquor from the preparation precipitates a yellow, amorphous substance (S, 9·1%), which behaves in the same manner as the methosulphate with solvents and in the preparation of the ferrichloride. The latter, namely, 7-*methoxy*-4-*phenylflavylium ferrichloride*, was prepared in the usual manner and crystallised from acetic acid in feathery, yellow needles, m. p. 191° (Found : C, 51·8; H, 3·1. $C_{22}H_{17}O_2Cl_4Fe$ requires C, 51·7; H, 3·3%). The salt was prepared for comparison from 7-hydroxy-2 : 4-diphenylbenzopyranol dimethyl ether (Bülow and Sicherer, *Ber.*, 1901, **34**,

2380), and a mixture of the specimens melted at 190—191°. The m. p., 185°, previously given for this ferrichloride (Crabtree, Robinson, and Turner, J., 1918, **113**, 877) is too low. This substance gives a negative result in a Zeisel estimation, probably on account of the insolubility of the iodide, and after the addition of phenol the production of methyl iodide could be observed.

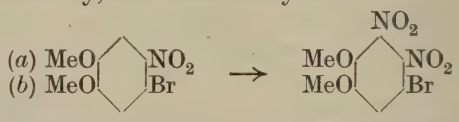
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THE UNIVERSITIES OF ST. ANDREWS AND MANCHESTER. [*Received, April 6th,* 1925.]

CCXII.—*The Nitration of* m-*Meconine.*

By JNANENDRA NATH RÂY and ROBERT ROBINSON.

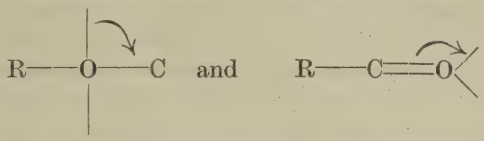
IN 1917 Jones and Robinson (J., **111**, 905) directed attention to a number of benzene substitution reactions which appeared to show that when two identical groups such as alkyloxy coexist in a molecule and direct substituents to different positions, the influence of the one which is in the *o*- or *p*-position to a negative * group is weakened so that the other alkyloxy- or similar group controls the direction taken by the reaction. For example, in the nitration of 4-bromo-5-nitroveratrole, the nitro-group diminishes the directive power of the methoxyl (*b*) in the *p*-position to a greater extent than that of (*a*) in the *m*-position and therefore the latter induces substitution, apparently abnormally, ortho to nitroxyl.



The criticisms of this hypothesis which have since been published have all been vitiated by the failure to recognise that the directing groups corresponding to (*a*) and (*b*) must be *identical* and therefore have been ignored, but, nevertheless, the development of the electronic theory of conjugation, whilst supplying the explanation of the phenomenon, also suggests a restriction to be placed on its scope. One of the most fundamental properties of oxygen and nitrogen, exhibited in carbon compounds, is expressed in terms of the electronic theory in the statement that bivalent oxygen and

* At the time, such groups as NO_2, CO_2H, SO_3H were called negative, and this is, of course, still permissible if the general polarity is the circumstance which ought to be emphasised.

tervalent nitrogen tend to increase the covalency at their single bindings, especially when attached to unsaturated systems, whereas there is a tendency to reduce the covalency of doubly linked oxygen or nitrogen. The free electrons on the oxygen and nitrogen are diminished in number in the former case and augmented in the latter. These changes are represented by the schemes :



In the first case, the oxygen becomes charged positively and in the second negatively. Now in the carbethoxyl and acid amide groups these tendencies can co-operate without disturbance of the octets and this is sufficient to explain the failure of the ester group to

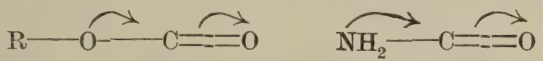


exhibit marked carbonyl reactivity and of the amide group to function as a strong basic centre. The positive charge on the carbon of the carbonyl group is neutralised from the chain and so does not seek foreign negative ions, whilst, in the amide group, the free electrons in the nitrogen octet are equally occupied in the chain to some extent; and it is these free electrons which impart the basic properties to ammonia. A similar neutralisation of the functions of groups like RO and C=O can occur if these are separated by an *even* number of unsaturated atoms (compare *Chemistry and Industry Review*, 1925, **44**, 18, 456), because in that case polarisation is possible without producing charges on intermediate atoms of the chain and without disturbing the octets.* We can therefore well understand the partial neutralisation of the directive power of methoxyl by a nitroxyl group situated in the *p*-position to it as shown in the annexed expression and, further, we suggest that the

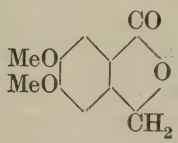


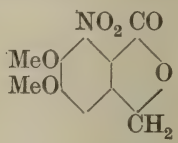
neutralisation considered by Jones and Robinson is always of this type. At present the effect can be predicted with confidence only when the directing group is derived from –OH, $-NH_2$, or –SH and

* We use the octet theory here, as always, in order to give a standard of numerical comparison. It does not affect the theory if the stable electronic configurations have more or less than 8 electrons, provided that the number tends to remain constant.

when the neutralising group is of the type $-NO_2$, –CO–R, etc. Certainly CO_2H is not such a group, being, as explained above, a self-contained assemblage. On the other hand, the carbonyl of phthalide is beyond doubt a more activating carbonyl than the carbonyl of an ordinary ester group. This is shown by condensation reactions of the methylene group in the ortho-position and on our theory means that the –CO–O– complex is not so completely satisfied in itself as it is in a typical ester. Therefore a similarly situated –CO–NH– should contain a more basic nitrogen atom than that of an ordinary amide; and this is the case, for phthalimidine has definite basic properties.

The opportunity to test this matter arose when Edwards, Perkin, and Stoyle (this vol., page 198) described an elegant synthesis of *m*-meconine (I) by the condensation of veratric acid with formaldehyde in presence of hydrochloric acid.

(I.) 



(II.)

As demanded by the theory which has been discussed above, this substance gives on nitration its 6-*nitro*-derivative (II), and we venture to suggest that such a result cannot be satisfactorily explained on any theory of the mechanism of aromatic substitution which is not based on electronic conceptions of valency. The constitution of (II) was proved by its conversion into a corresponding *bromo*-m-*meconine*, which is also obtained by applying the method of Edwards, Perkin, and Stoyle to 2-bromoveratric acid, the orientation of the groups in the molecule of which has been placed beyond question. Hope and Robinson (J., 1911, **99**, 1163) showed that phthalide contains a reactive $-CH_2-$, because it condenses with cotarnine to form anhydrocotarninephthalide. The poor yield was improved and became almost quantitative when a nitroxyl was introduced into the *o*- or *p*-position to the methylene group. The condensation is also facilitated, although to a less striking extent, when a nitroxyl group is introduced in the *m*-position to the methylene group (compare P., 1911, **27**, 229). A new example of this phenomenon is now forthcoming, since we are able to prepare *anhydrocotarnine-nitro*-m-*meconine* by a direct condensation of the components indicated.

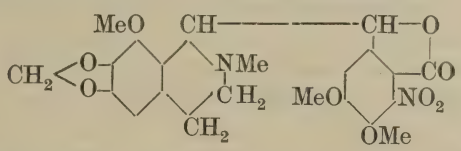
Experimental.

Preparation of m-*Meconine* (I).—The method of Edwards, Perkin, and Stoyle (*loc. cit.*) gives improved yields if the following slight

modification is adopted. A solution of veratric acid (50 g.) in hot acetic acid (250 c.c.) is, after the introduction of concentrated hydrochloric acid (200 c.c.) and aqueous formaldehyde (60 c.c. of 40%), heated on the steam-bath for 12 hours, cooled, tarry matter precipitated by the addition of a little water, and the brown liquid treated with charcoal, filtered, and concentrated in a vacuum to about one-fifth of its volume. Further tarry material is precipitated from the hot solution by addition of not too much water, and, after filtration, *m*-meconine is thrown down by further dilution with water and neutralisation with sodium carbonate. The *m*-meconine, crystallised from aqueous ethyl alcohol, has m. p. 155° and the yield averages 30 g.

6-*Nitro*-4 : 5-*dimethoxyphthalide* (II).—*m*-Meconine (13 g.) was gradually added with agitation to nitric acid (22 c.c.; *d* 1·42) at 0°; after a few hours the mixture was added to water, and the precipitate collected and extracted with boiling alcohol (30 c.c.). The residue crystallised from boiling acetic acid in colourless needles, m. p. 183—184° (yield 6—7 g.) (Found: C, 50·4; H, 3·4. $C_{10}H_9O_6N$ requires C, 50·2; H, 3·7%). This substance is sparingly soluble in hot alcohol and exhibits the behaviour of a lactone. Unlike nitromeconine, it does not give an intense coloration on treatment with hot alkaline solutions and this is clearly due to the fact that the methylene and nitroxyl groups are in the *m*-position to each other.

Anhydrocotarnine-6-*nitro*-4 : 5-*dimethoxyphthalide*,



—A mixture of nitro-*m*-meconine (3 g.), cotarnine (3 g.), and ethyl alcohol (300 c.c.) was boiled for 1·5 hours and then concentrated to one-fourth of its bulk and cooled. The crystalline deposit was isolated, treated with glacial acetic acid, and, after dilution with water and filtration, the base was precipitated by means of ammonia, collected, washed, and dried (2·5 g.). The base is very sparingly soluble in most neutral organic solvents and is best crystallised from boiling toluene–alcohol, from which it separates in well-defined, rectangular plates, m. p. 200° (decomp.) (Found: C, 57·8; H, 4·7, 4·8, 5·5; $C_{22}H_{22}O_9N_2$ requires C, 57·6; H, 4·8%). The base is readily soluble in dilute hydrochloric acid and acetic acid to a colourless solution. It is stable to hot dilute hydrochloric acid, but is gradually decomposed by boiling acetic acid with formation of cotarninium acetate

and nitro-*m*-meconine. It is, however, much more stable to hot acetic acid than anhydrocotarnine-nitromeconine; ease of formation and ease of decomposition going together in this series as in most others.

6-*Amino*-4 : 5-*dimethoxyphthalide*.—Nitro-*m*-meconine (11 g.) was gradually added to a hot solution of crystallised stannous chloride (35 g.) in concentrated hydrochloric acid (65 c.c.), when a clear liquid resulted, and the reaction was completed by heating on the steam-bath for 30 minutes. After dilution with water (250 c.c.) the cooled solution deposited crystals, which were isolated and treated with sodium bicarbonate in hot aqueous suspension. The substance crystallised from aqueous alcohol in colourless, feathery needles, m. p. 158° (yield about 6 g.) (Found: C, 57·0; H, 5·3. $C_{10}H_{11}O_4N$ requires C, 57·4; H, 5·3%). The amine is readily soluble in concentrated hydrochloric acid, but is precipitated on the addition of water. In suspension in dilute hydrochloric acid it can be diazotised, giving a bright yellow diazonium salt, which couples with β-naphthol to form a red azo-compound.

6-*Bromo*-4 : 5-*dimethoxyphthalide*.—(A) A solution of amino-*m*-meconine (6 g.) in 6% hydrochloric acid (60 c.c.) was diazotised at 0° and added to a solution of cuprous bromide (prepared from 2·4 g. of copper sulphate, potassium bromide and sulphur dioxide) in hydrobromic acid (4 c.c.; *d* 1·49). The reaction was completed by heating, and, after cooling, the precipitated solid was collected and crystallised from boiling water containing a little alcohol. The almost colourless, prismatic needles had m. p. 223°, alone or mixed with a specimen prepared by the following method.

(B) A mixture of 2-aminoveratric acid (7·1 g.) (Pschorr and Sumuleanu, *Ber.*, 1899, **32**, 3410), water (50 c.c.), and concentrated hydrochloric acid (10 c.c.) was treated at 0° with sodium nitrite (2·7 g. in water, 20 c.c.), the clear diazo-solution added to one of cuprous bromide (from 2·4 g. of copper sulphate) in hydrobromic acid (4 c.c.; *d* 1·49), and the reaction completed by heating on the steam-bath, evolution of nitrogen being first observed at 80°. The crude 2-bromoveratric acid which separated on cooling was crystallised from hot aqueous acetic acid and had m. p. 200° (yield 4—5 g.). Zincke and Francke (*Annalen*, 1896, **293**, 187) give m. p. 201°, their initial material being hemipinimide (compare Kühn, *Ber.*, 1895, **28**, 810).

A mixture of 2-bromoveratric acid (4 g.), aqueous formaldehyde (5·5 c.c. of 40%), concentrated hydrochloric acid (20 c.c.), and acetic acid (30 c.c.) was heated on the steam-bath during 10 hours. The product was added to water (250 c.c.), the precipitate of unchanged acid removed, and the filtrate concentrated to about 50 c.c. in a

vacuum and then neutralised with solid sodium bicarbonate. The solid which gradually separated crystallised from boiling water containing a little alcohol in colourless, prismatic needles, m. p. 223° (Found: C, 44·3; H, 3·1. $C_{10}H_9O_4Br$ requires C, 43·9; H, 3·3%).

THE UNIVERSITY, MANCHESTER. [*Received, May 13th*, 1925.]

CCXIII.—*The System Sodium Sulphite–Sodium Hydroxide–Water.*

By DALZIEL LLEWELLYN HAMMICK and JOHN ALEXANDER CURRIE.

A STUDY of this system was undertaken in order to find out the nature of the solid phases in equilibrium with solutions containing sodium sulphite and hydroxide. As our object was this, rather than the exact form of the solubility curve showing the amount of solids in solution, we did not aim at an accuracy of more than $\pm$ 0·5% in our analyses.

Sodium sulphite was prepared by passing sulphur dioxide into a solution of A.R. sodium carbonate (The British Drug Houses), precautions being taken throughout that air should not come into contact with the solution. Slightly more sulphur dioxide was passed in than would be sufficient to form the sulphite, in order to eliminate the danger of a double salt of sulphite and carbonate crystallising. Any hydrogen sulphite that might thus be formed would be turned into the normal salt when mixed with the soda solution in the solubility vessel. In practice, it was found that the normal salt came down under these conditions. The solution thus prepared was transferred, in contact with hydrogen only, to an electrically heated glass evaporator through which was passed a current of purified hydrogen. When a good crop of crystals had been deposited, the liquid was drained off, the crystals were washed and dried in an atmosphere of hydrogen, and stored in a vacuum desiccator over soda sticks.

The salt was tested for sulphate and rejected if any was found to be present. It was then analysed as sulphate, no specimen being used that had SO_3 lower than 63·2%, theory requiring 63·47%.

Sodium hydroxide. For the preparation of solutions up to 20% NaOH Cornog's method was used (*J. Amer. Chem. Soc.*, 1921, **43**, 2573). For stronger solutions we took advantage of the fact that from very strong solutions of sodium hydroxide nearly all the carbonate present is precipitated (Freeth, *Phil. Trans.*, 1922, **223**, 35). By allowing saturated solutions of the best soda sticks (The British

Drug Houses) to reach equilibrium at a temperature slightly above that of the isotherm we were studying, we obtained a solution of sodium hydroxide on filtering that was as strong as we required and that gave no precipitate with barium chloride solution. The suspensions complained of by Freeth were not observed, the solution being quite clear after filtering through Gooch asbestos.

Water. All water used in preparing the materials and making up solutions was distilled and then boiled under reduced pressure for ½ hour.

Solubility Determinations.—Complexes of approximately known composition were made up in one of two kinds of vessel. When the strength of the sodium hydroxide in solution did not exceed 25%, we used very wide test-tubes of Duro resistance glass closed by tight-fitting rubber stoppers through which a stirrer passed, fitted with a mercury seal. For stronger solutions, a silver vessel was employed similar to that used by Freeth (*loc. cit.*). Glycerol was used as a seal and lubricant, precautions being taken that none of it should leak into the solution.

The vessels were placed in an ordinary gas-regulated thermostat for the isotherms at 20°, 25°, and 32°, the temperature of which did not vary by more than $\pm 0{\cdot}1°$. For the isotherm at 0·15°, ice was placed in a well-lagged thermostat, and kept near the bottom with wire netting. The thermostat was then filled with water and kept well stirred; by this means and by renewing the ice every 48 hours the temperature never varied by more than 0·05°.

After equilibrium had been obtained—about 24 hours for weak solutions and 36—48 for strong ones was found to be sufficient—the contents of the vessel were rapidly transferred to a filter. This was so designed that the separation of the solution and moist solid could be carried out in the thermostat, a precaution found to be necessary when the soda content of the solution was either very weak or very strong. The whole operation was carried out as rapidly as possible.

Analysis.—After they had been weighed, the solutions and moist solids were made up in water to suitable volumes, portions of which were analysed. The sulphite was first oxidised to the sulphate by treatment with pure hydrogen peroxide solution and after standing a short time the excess of peroxide was decomposed by boiling. The sulphite was then estimated as barium sulphate and the hydroxide by titration, the water being obtained by difference. The results were plotted by the usual Schreinemakers method on a triangular diagram (see Figs. 1 and 2).

Results.—The isotherms at 0·15° and 32° are shown in the diagrams. The isotherms at 20° and 25°, being of the same general

form as that at 0·15°, have not been shown. The figures are given below. Compositions are given in weight per cent.

Isotherm at 0·15°.

Liquid.		Residue.		Composition of solid phase in water.
NaOH.	Na_2SO_3.	NaOH.	Na_2SO_3.	
—	12·2*	—	—	$Na_2SO_3,7H_2O$
3·0	9·0	0·8	43·9	,,
9·0	5·2	1·9	41·3	,,
16·9	2·8	2·4	44·5	,,
21·9	2·21	2·3	44·9	,,
23·3	2·2	3·7	55·3	$Na_2SO_3,7H_2O$ and Na_2SO_3
25·4	1·3	6·4	76·0	Na_2SO_3
26·6	0·7	3·6	87·5	,,
27·1	0·4	6·6	75·3	,,
27·9	0·1	—	—	,,
29·1	0·1	35·5	0·9	Na_2SO_3 and $NaOH,4H_2O$
29·5†	—	—	—	$NaOH,4H_2O$

Isotherm at 20°.

—	21·2*	—	—	$Na_2SO_3,7H_2O$
1·6	18·7	0·3	47·4	,,
4·4	15·4	—	—	,,
8·3	12·0	—	—	,,
9·9	11·0	3·3	37·4	,,
11·6	9·9	—	—	,,
12·2	9·6	—	—	,,
12·7	9·4	—	—	,,
13·4	9·2	—	—	,,
14·0	9·0	0·2	68·3	$Na_2SO_3,7H_2O$ and Na_2SO_3
13·8	8·6	1·1	77·4	,, ,,
15·5	7·0	1·0	95·5	Na_2SO_3
16·0	6·7	3·8	87·0	,,
20·2	3·5	—	—	,,
24·9	1·1	—	—	,,
26·8	1·0	—	—	,,
36·3	0·1	5·6	85·2	,,
50·1	Trace	8·3	82·1	,,
52·2†	—	—	—	$NaOH,H_2O$

Isotherm at 25°.

—	23·6*	—	—	$Na_2SO_3,7H_2O$
0·7	22·5	—	—	,,
2·5	19·3	0·3	48·4	,,
5·0	17·7	0·8	47·1	,,
9·7	13·0	1·7	42·1	,,
9·8	13·2	0·1	56·3	$Na_2SO_3,7H_2O$ and Na_2SO_3
9·6	13·8	0·7	92·8	,, ,,
12·2	10·2	0·5	95·1	Na_2SO_3
12·6	10·1	—	—	,,
14·2	8·2	—	—	,,
17·2	5·8	—	—	,,
20·7	2·9	2·9	86·8	,,
20·7	2·5	—	—	,,
25·2	1·0	—	—	,,
28·7	0·5	—	—	,,
29·4	0·3	—	—	,,
42·7	0·1	—	—	,,
43·9	Trace	—	—	,,
53·3†	—	—	—	$NaOH,H_2O$

* Lewis and Rivett, J., 1924, **125**, 1156. † Pickering, J., 1893, **63**, 890.

Isotherm at 32°.

Liquid.		Residue.		Composition of solid phase in water.
NaOH.	Na_2SO_3.	NaOH.	Na_2SO_3.	
—	26·5*	—	—	Na_2SO_3
0·6	26·4	—	—	,,
2·3	23·1	0·1	89·0	,,
5·1	19·1	0·1	89·0	,,
7·6	15·7	—	—	,,
11·1	11·2	0·8	93·6	,,
16·5	5·4	0·8	95·4	,,
20·1	2·9	2·1	90·5	,,
27·2	0·6	2·3	92·0	,,
36·2	0·1	6·0	83·1	,,
51·8	0·001	9·0	81·6	,,
54·4†	—	—	—	$NaOH,H_2O$

* Lewis and Rivett, J., 1924, **125**, 1156. † Pickering, **J.**, 1893, **63**, 890

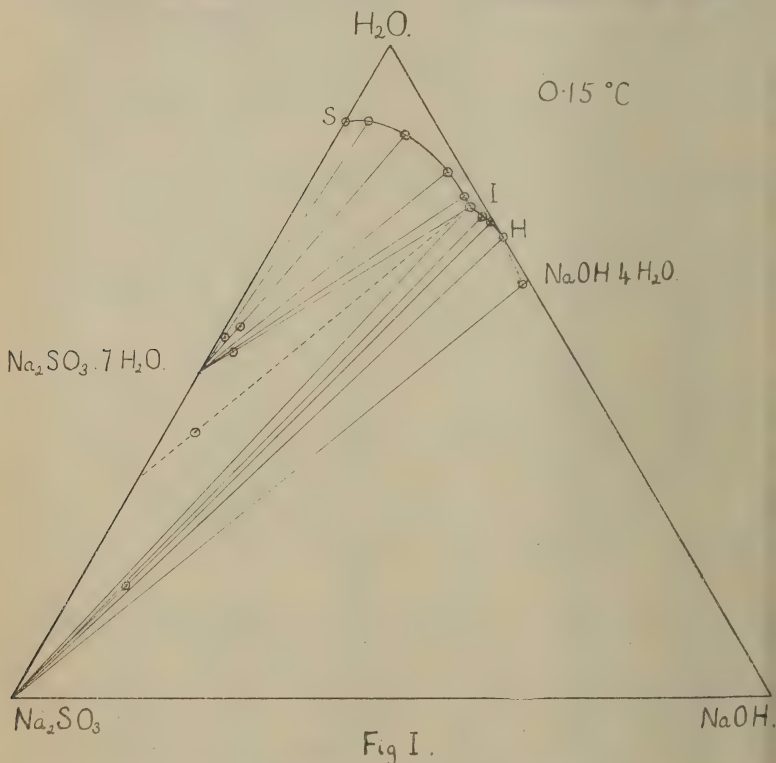


Fig I.

The isotherm at 0·15° is shown in Fig. I. The results obtained at 20° and at 25° give curves resembling Fig. I except that the heterogeneous region $Na_2SO_3,7H_2O$–S–I becomes smaller; in this region complexes separate into solutions of concentrations along S-I and sodium sulphite heptahydrate. Solutions of compositions given by I–H are in equilibrium with anhydrous sodium sulphite. The

point H, which lies very close to the side H_2O–NaOH (the solubility of sulphite being very small in excess of sodium hydroxide) represents the composition of the liquid in equilibrium with anhydrous sodium sulphite and sodium hydroxide tetrahydrate. Similar points were not realised experimentally at the other temperatures.

The isotherm at 32·0° (Fig. II) shows that at that temperature sodium sulphite heptahydrate cannot exist in contact with any aqueous solution. This is in accordance with the results obtained by Lewis and Rivett (J., 1924, **125**, 1156), who found the transition

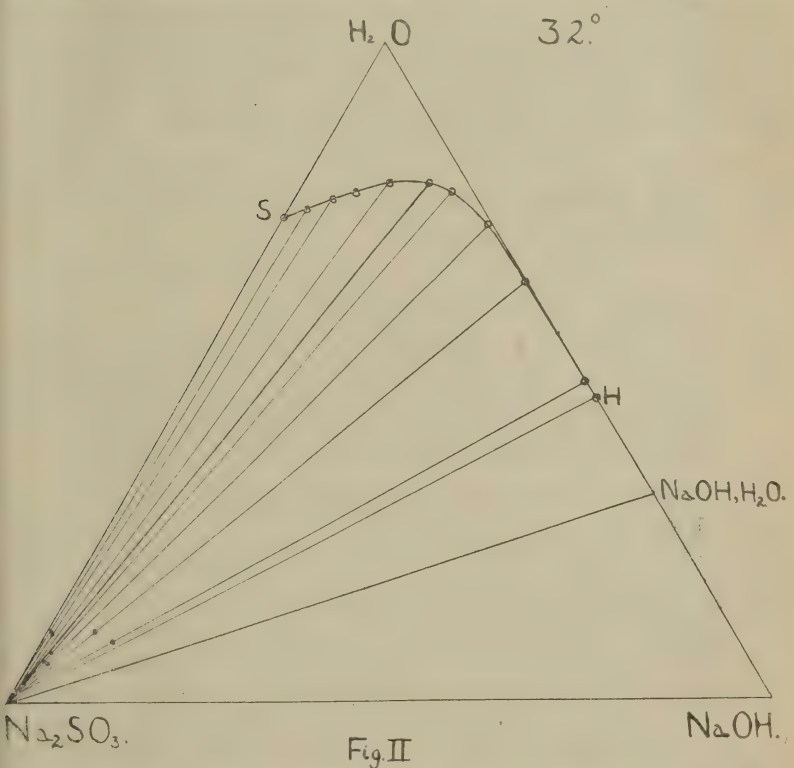


Fig. II

point between anhydrous and hydrated sodium sulphite to lie at 31·5°. The fact that heptahydrate appeared as a solid phase in the isotherm at 25° is in conflict with the result obtained by Hartley and Barrett (J., 1909, **95**, 1178), who record 22° as the transition point. Recently, however, Foerster, Brosche, and Norberg-Schulz (*Z. physikal. Chem.*, 1924, **110**, 450), as the result both of solubility measurements and dilatometer experiments, have concluded that the transition point lies at 33·4°.

The above discrepancies seem at first sight hard to reconcile.

Lewis and Rivett (*loc. cit.*) have, however, established the fact that anhydrous sulphite may exist in more than one metastable solid phase, particularly in the presence of sodium sulphate, which appears in solid solution in the sulphite crystals. Different solid phases in equilibrium would readily account for the comparatively small difference between the transition point found by Foerster and by Lewis and Rivett. Moreover, the latter workers record (*loc. cit.*, p. 1166) a temperature of 39° as the transition point between one form of anhydrous sulphite and the hydrated form ; this temperature is almost as much above Rivett and Lewis's value for their most stable form as Barrett and Hartley's is below. It therefore does not seem impossible that Barrett and Hartley really obtained the most stable form of anhydrous sulphite and that their transition temperature of 22° represents the true transition point.

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THE DYSON PERRINS LABORATORY,
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CCXIV.—*Oxidation Products of Oleic Acid. Part I. Conversion of Oleic Acid into Dihydroxystearic Acid and the Determination of the Higher Saturated Acids in Mixed Acids from Natural Sources.*

By ARTHUR LAPWORTH and EDWARD NEVILLE MOTTRAM.

THE authors have suggested that an accurate estimation of higher saturated acids in a sample of oleic acid might be carried out by oxidation methods (*Biochem. J.*, 1925, **19**, 17, footnote).

Hazura and Grüssner (*Monatsh.*, 1888, **8**, 180) were able to detect oleic acid in mixtures by oxidising it to dihydroxystearic acid. Edmed (J., 1898, **73**, 627), Le Sueur (J., 1901, **79**, 1313), and Nicolet (*J. Amer. Chem. Soc.*, 1922, **44**, 1139) investigated the conversion of oleic into dihydroxystearic acid, but obtained results which clearly indicate that their experiments were not made under very favourable conditions. Edmed (*loc. cit.*) stated that practically quantitative yields of the dihydroxy-acid can sometimes be obtained, but unfortunately gave no clue to the necessary conditions.

Robinson and Robinson (this vol., p. 177) obtained excellent yields of the dihydroxy-acid by oxidising in dilute alkaline solution at 0°. Based on that observation, privately communicated some three years ago, a long series of systematic experiments has been carried out by the present authors and it is now possible to state

that the conditions essential for the nearly perfect conversion of oleic acid into dihydroxystearic acid are: (1) a low temperature (0—10°) during the oxidation process; (2) a concentration of oleic acid (in the form of its sodium or potassium salt) not exceeding 0·1%; (3) a concentration of the added aqueous permanganate solution not exceeding 1%; (4) a very short period of reaction, 5 minutes being sufficient for oxidation of nearly the whole of the oleic acid present; * (5) a slight excess of alkali should be present from the beginning of the oxidation, otherwise there is a danger of hydroxyketostearic acid being formed.

The observations can be applied to the analysis of comparatively impure samples of oleic acid, and in particular to the estimation of the proportion of all saturated fatty acids which are not volatile in steam, as, for example, stearic, palmitic and myristic acids. Even when much linolic or linolenic acid is present, their oxidation products (namely tetrahydroxy- and hexahydroxy-stearic acids) being insoluble in cold light petroleum and their degradation products either insoluble in light petroleum or volatile in steam, it seems probable that the method can be modified so as to afford a simple means of isolating the higher saturated fatty acids present in the mixed acids from many natural sources.

Detailed Analytical Method.†—The clear solution of sodium salts obtained by warming about 5 g. of the "oleic acid" on the water-bath with an equal weight of caustic soda, dissolved in 500 c.c. of water, is cooled, 4 litres of ice-cold water are added, and the whole is well shaken at 10° while 400 c.c. of 1% potassium permanganate solution are added quickly. After 5 minutes, the liquid is decolorised with sulphur dioxide, and concentrated hydrochloric acid (150 c.c.) added. The white, flocculent precipitate (A) of crude solid dihydroxystearic acid is drained for a short time, washed with about 50 c.c. of light petroleum (this greatly accelerates its subsequent drying: the petroleum washings are reserved),‡ and dried to a constant weight at the ordinary temperature in a vacuum desiccator.

* It is not desirable to submit the resulting dihydroxystearic acid to further action of the permanganate, and if it is desired to obtain the most precise results, a further conversion of the very small quantity of unchanged oleic acid is necessary and it is best to proceed as hereinafter described. For many purposes the results obtained by omission of the second oxidation process would be accurate enough.

† The solubility of dihydroxystearic acid in petroleum (b. p. 80—100°) is not more than 0·002 g. in 100 c.c. at 15°, and therefore negligible in applying this method.

‡ The aqueous filtrate contains no appreciable quantities of higher fatty acids, but does contain about 0·15 g. of products of lower molecular weight, such as nonoic, octoic, azelaic and suberic acids, formed by breaking down of a small fraction of the dihydroxystearic acid.

It is now extracted with 100—150 c.c. of warm light petroleum (b. p. about 70—80°), the whole cooled, filtered, and the residue (B) of nearly pure dihydroxystearic acid washed with several successive quantities of cold solvent. The petroleum extracts and washings are united and evaporated.*

The residue left on evaporation of the petroleum extracts is distilled with steam to remove traces of volatile fatty acids, and treated with low-boiling petroleum. This readily extracts the non-volatile acids, which, after evaporation of the solvent, are heated on the water-bath until constant in weight. On cooling, the residue (D) sets to a waxy solid and represents the higher saturated fatty acids present in the original sample of " oleic acid." †

Examples.—(1) A sample of oleic acid, O_1, was isolated from olive oil and purified through the barium salt (Lapworth and Mottram, *loc. cit.*). Its " first setting-point " (*loc. cit.*) was 12·55° and a break in the setting-point curve of its mixtures with pure palmitic acid took place with 4·7% of added palmitic acid. As the break corresponds with a total percentage 7·2 $\pm$ 0·5 of palmitic acid, O_1 consisted of 97·5 $\pm$ 0·5% of oleic acid and 2·5 $\pm$ 0·5% of palmitic acid.

Results of analyses by the above method : (*a*) 4·97 g. and (*b*) 3·06 g. of O_1 gave 0·1 g. and 0·07 g., respectively, of higher saturated acids, or 2·0 and 2·25%.

These three results agree very satisfactorily with one another. The weight of dihydroxystearic acid, free from fatty acids, obtained in (*a*) was 5·23 g. or 96% of the calculated amount (5·45 g.) from the 4·87 g. of pure oleic acid present. In case (*b*) the weight was again 95—96% of the calculated quantity. The loss of 4% was in part accounted for by the presence of 0·09 g. of azaleic (or suberic) acid, which, in case (*a*), was actually isolated from the aqueous filtrate and had evidently arisen by further oxidation of part of the dihydroxystearic acid.

* In order to effect, if desired, a complete conversion of the small quantity of oleic acid which still remains, the residue left on evaporation of the petroleum is oxidised as described above : 50 c.c. of cold *N*/10-sodium hydroxide and 100 c.c. of ice water; 15 c.c. of 1% potassium permanganate solution; 10 c.c. of concentrated hydrochloric acid. The precipitate (C) is washed with water, dried at the ordinary temperature, and extracted with cold light petroleum; about 0·05 g. of dihydroxystearic acid remains on the filter.

† " Non-saponifiable " constituents in the original sample are not, in the authors' experience, to be found in the residue (D), at least not in appreciable quantity. If thought desirable, however, the quantity of such constituents can easily be determined by the usual method, or perhaps more simply by dissolving the residue (D) in a little methyl alcohol, adding excess of methyl-alcoholic barium hydroxide, evaporating to complete dryness, and extracting the residue with dry acetone, in which barium hydroxide and barium salts of saturated fatty acids are insoluble.

The "saturated fatty acid," as isolated, melted at 57°, and doubtless consisted mainly of palmitic acid (m. p. 62·5°).

(2) *Total mixed acids from olive oil.* Olive oil was completely hydrolysed and the resulting mixed acids (O_2) were isolated. These had an iodine number = 88 and contained 1·4% of "unsaponifiable matter."

5·0 G. of O_2, treated as above described, gave 0·78 g. of higher saturated fatty acids (waxy, pale yellow solid, m. p. 53—54°) or 15·6%. On the assumption, then, that O_2 contained only the following constituents, its composition was roughly: Oleic acid, 72; linolic acid, 12—13; unsaponifiable matter, 1·4; higher saturated acids, 14—15%.* The total weight of dihydroxystearic acid isolated was 4·1 g. This doubtless contained tetrahydroxystearic acid arising from the linolic acid present, and other experiments have shown it to be purely fortuitous that this weight again represents 96% of the weight of dihydroxystearic acid theoretically obtainable from the oleic acid estimated as present in the mixed acids.†

The "unsaponifiable matter" in the 0·78 g. of higher saturated fatty acids, determined by the methyl-alcoholic baryta method (footnote, p. 1630), was a negligible quantity (only 0·02 g.).

(3) A sample of a commercial product sold as "pure oleic acid" yielded 16% of solid saturated fatty acids; but the weight of "dihydroxystearic acid" was very appreciably less (only 3·4 g. from 5 g.) than in the case of example (2). The manipulations offered no greater difficulties than in the previous cases.

The work described in the present paper was begun under the auspices of the Oils and Fats Committee of the Food Investigation Board. A grant from the Department of Scientific and Industrial Research to one of us (E. N. M.) rendered it possible for him to take part in the research and is gratefully acknowledged.

THE UNIVERSITY, MANCHESTER. [*Received, May 5th,* 1925.]

* The main object of the experiment was to ascertain whether the presence of so much linolic acid would affect the ease of filtration of the crude hydroxystearic acid, and from this point of view the results were all that could be desired. It now seems probable that estimates formed by previous workers of the proportion of oleic acid in the mixed acids from olive oil have been decidedly too high and those of the saturated fatty acids too low. This conclusion is also consistent with the experience which the writers had previously had in analyses of fractions of lead salts made in purifying oleic acid.

† Judging from the results of experiments which the authors have made on the production of hydroxyketostearic acid, the yield of dihydroxystearic acid may fall off very rapidly if the proportion of acids more highly unsaturated than oleic acid exceeds a certain maximum.

CCXV.—*The Action of Hydrogen Peroxide on Limonene.*

By James Sword.

The oxidation of limonene with hydrogen peroxide (2 mols.) in acetic acid solution gives $\Delta^{8(10)}$-*p*-menthene-1 : 2-diol as the main product, a small yield of terpin hydrate, an aldehyde, etc. Larger quantities of the oxidising agent produce a variety of oxygenated compounds and resinous substances.

Since hydrogen peroxide has no action on hydrocarbons of the terpene series in solvents such as ether, it would appear that acetic acid takes a real part in the reaction, possibly by the formation of peracetic acid. This is supported by the fact that the reaction proceeds more quickly the larger the quantity of solvent used; a certain minimum amount is necessary for the reaction to go to completion in any length of time.

Experimental.

The limonene used was obtained from oil of bitter orange (J., 1907, **91**, 1872) and had b. p. 175·5—176·5°, $[\alpha]_D^{15°}$ + 96·89°, $d^{15°}$ 0·8453, $n^{15°}$ 1·4759.

100 C.c. of it in glacial acetic acid (375 c.c.) were shaken continuously for 14—18 days with perhydrol, added gradually (total 180 c.c.). The solution was neutralised with sodium carbonate, and extracted with ether, on occasions up to 40 times. The extract on concentration deposited about 1 g. of terpin hydrate, m. p. 116—117° (in a sealed tube) (Found: C, 62·8; H, 11·5%), and on evaporation left an oil, which was hydrolysed with methyl-alcoholic barium hydroxide, yielding an oil (*a*). This, on distilling under reduced pressure, gave three fractions: (i) a mobile oil, b. p. 110—112°/10 mm., (ii) the main fraction, a viscous oil, b. p. 140—143°/10 mm., from which a glycol (*b*) was isolated, (iii) a semi-vitreous solid, b. p. 150—152°/10 mm. These were all unsaturated, the unsaturation decreasing with increase of boiling point, and gave sodium derivatives [Found: for (i), Na, 9·5; for (ii), Na, 22·7; for (iii), Na, 16·1. $C_{10}H_{16}(ONa)_2$ requires Na, 21·3%. $C_{10}H_{17}\cdot ONa$ requires Na, 13·0%].

By using the residual oil from the preparation of the sodium compounds (only a small quantity of sodium was used for a relatively large amount of oil) the glycol (*b*) was finally induced to crystallise. Thereafter it could be crystallised directly from (*a*). The residual oil after its removal yielded a small quantity of a *p*-nitrobenzoate, m. p. 79°, gave with ethereal hydrogen bromide a dihydrobromide which crystallised from ethyl alcohol in pearly plates, m. p. 44—45° (Found: Br, 53·5. $C_{10}H_{16},2HBr$ requires

Br, 53·6%), and on distillation with steam yielded an unsaturated oil (Found: C, 72·0; H, 9·9%. 0·1818 G. absorbed 0·165 g. of bromine), from which no nitrobenzoate was obtained, and no solid on hydration.

The glycol (*b*) is soluble in about 10 parts of water and much more soluble in alcohol or ether. It will crystallise only when hydrated. The hydrate is efflorescent and contains three molecules of water, all of which can be removed over sulphuric acid in a vacuum desiccator in the course of 4—5 days. If dried too rapidly, it liquefies and then sets to a hard, vitreous solid. This, in conjunction with the fact that the hydrate has no definite melting point but begins to melt about 20° below the melting point of the anhydrous substance, indicates that there is an intermediate hydrate of lower melting point. Its solution in alcohol is optically inactive. The anhydrous substance is snow-white, melts sharply at 67·5°, and is clearly the $\Delta^{8(10)}$-*p*-menthene-1 : 2-diol described by Prileschaev (*Ber.*, 1909, **42**, 4814) (Found: C, 70·6; H, 10·5. Calc., C, 70·6; H, 10·7%).

From the original oxidation products a small quantity of an acid was isolated by means of its silver salt [Found: Ag, 55·4. $C_6H_{12}(CO_2Ag)_2$ requires Ag, 55·7%.]

The author wishes to acknowledge his indebtedness to Professor G. G. Henderson for his interest in the work.

The University of Glasgow. [*Received, April 28th,* 1925.]

CCXVI.—*Hydroxybenzils.*

By John Thompson Marsh and Henry Stephen.

Schönberg and his collaborators (*Ber.*, 1922, **55**, 1174, 3746, 3753) have shown that the oxidation of benzoins gives rise to benzils of two types, *viz.*, yellow compounds of the normal type, having the α-diketonic structure and characteristic properties, and colourless ψ-benzils, to which Schönberg ascribes a peroxidic structure which accounts for their slight reactivity towards the usual ketonic reagents.

Up to the present, few examples of colourless benzils were known (compare Irvine, J., 1907, **91**, 541; Vörlander, *Ber.*, 1911, **44**, 2455; Schönberg and Kraemer, *loc. cit.*, p. 1174; Schönberg and Malchow, *loc. cit.*, p. 3748) and only in one case, 4 : 4′-dibenzyloxybenzil, has the coloured diketone been converted into the colourless peroxide (Schönberg and Bleyberg, *loc. cit.*, p. 3753), and the latter, by

crystallisation from various solvents, reconverted into the coloured benzil. Schönberg therefore regards the two forms as being in equilibrium both in solution and at the melting point:

$$RO\cdot C_6H_4\cdot\underset{\underset{O}{|}}{C}—\underset{\underset{O}{|}}{C}\cdot C_6H_4\cdot OR \rightleftharpoons RO\cdot C_6H_4\cdot\underset{\underset{O—O}{|\quad|}}{C=C}\cdot C_6H_4\cdot OR.$$

By applying Hoesch's method of synthesising aromatic hydroxyketones (*Ber.*, 1915, **48**, 1122) to acyl cyanides and resorcinol and phloroglucinol, we have prepared the eight following colourless hydroxybenzils; the colours produced when they are dissolved in concentrated sulphuric acid are recorded:

2 : 4-Dihydroxybenzil, $C_6H_3(HO)_2\cdot CO\cdot COPh$, red.
2 : 4-Dihydroxy-2′-methoxybenzil, $C_6H_3(HO)_2\cdot CO\cdot CO\cdot C_6H_4\cdot OMe$, greenish-brown.
2 : 4-Dihydroxy-4′-methoxybenzil, $C_6H_3(HO)_2\cdot CO\cdot CO\cdot C_6H_4\cdot OMe$, purple.
2 : 4-Dihydroxy-3′ : 4′ : 5′-trimethoxybenzil, $C_6H_3(HO)_2\cdot CO\cdot CO\cdot C_6H_2(OMe)_3$, blue.
2 : 4 : 6-Trihydroxybenzil, $C_6H_3(HO)_3\cdot CO\cdot COPh$, red.
2 : 4 : 6-Trihydroxy-2′-methoxybenzil, $C_6H_2(HO)_3\cdot CO\cdot CO\cdot C_6H_4\cdot OMe$, reddish-brown.
2 : 4 : 6-Trihydroxy-4′-methoxybenzil, $C_6H_2(HO)_3\cdot CO\cdot CO\cdot C_6H_4\cdot OMe$, purple.
2 : 4 : 6-Trihydroxy-3′ : 4′ : 5′-trimethoxybenzil, $C_6H_2(HO)_3\cdot CO\cdot CO\cdot C_6H_2(OMe)_3$, greenish-blue.

With the exception of the last, these compounds darken before melting with decomposition. This change is not due to conversion of peroxide into diketone, for the acetyl derivatives remain colourless above their melting points.

The hydroxybenzils crystallise from dilute alcohol or dilute acetic acid in colourless needles. Their pink solutions in aqueous sodium hydroxide, on warming, become deep red, and on acidification the benzils are precipitated as bright yellow needles, from which the colour does not completely disappear on crystallisation; the melting points, however, are identical with those of the colourless forms. We have so far not obtained a pure, stable, coloured form of the above colourless benzils.

On account of the action of the alkali, methylation of the hydroxybenzils was not successful. Attempts to demethylate those compounds containing methoxy-groups did not give very satisfactory results.

The trihydroxybenzils give a purple coloration with ferric chloride solution, but only a faint colour was noticed with the dihydroxy-compounds. Both di- and tri-hydroxybenzils reduce Fehling's solution.

The solutions of the hydroxybenzils in organic solvents are colourless even on boiling and are stable towards hydroxylamine, phenylhydrazine, *p*-nitrophenylhydrazine, semicarbazide, and *o*-phenylenediamine, and the hydroxybenzils do not undergo the benzilic acid transformation.

From these facts, the authors are of the opinion that these

compounds are peroxides both in the crystalline form and in solution.

Experimental.

Preparation of Acyl Cyanides.—The following method differs in certain details from that suggested by Claisen (*Ber.*, 1898, **31**, 1023) and utilised by Mauthner (*Ber.*, 1908, **41**, 921; 1909, **42**, 189) and is of general application. It is a great improvement on the method of heating acid chlorides with cyanides of heavy metals.

A solution of the acid chloride (1 mol.) and pure hydrogen cyanide (4 mols.) in dry ether (5 vols.) was cooled in ice while anhydrous pyridine (4 mols.) was added gradually during 1 hour, and the mixture kept in ice-water for 12 hours. The pyridine hydrochloride was removed by filtration, and the ether and excess of pyridine by distillation, the latter under diminished pressure, and the residue of cyanide, having been freed from traces of pyridine hydrochloride by filtration in ethereal solution, was either distilled or crystallised.

This method avoids treatment with water and thereby eliminates any possibility of hydrolysis of the cyanide, to which the majority of the acyl cyanides are prone. In the cases investigated, the cyanides were usually sufficiently pure for condensation after evaporation of the ether. The yields are good.

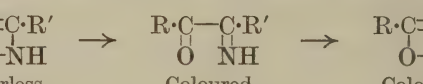
Benzoyl cyanide crystallises in pale yellow needles, m. p. 32°, from ligroin (compare Wöhler and Liebig, *Annalen*, 1832, **3**, 267).

o-*Methoxybenzoyl Cyanide.*—To prepare the requisite chloride, *o*-methoxybenzoic acid (1 mol.) was dissolved in thionyl chloride (1½ mols.) and the solution subsequently warmed on the water-bath for ½ hour; the excess of thionyl chloride was removed under diminished pressure, and the acid chloride distilled; b. p. 136°/12 mm. The duration of heating should not be longer than that stated, since thionyl chloride tends to demethylate the acid chloride. The same remarks apply to the preparation of *p*-methoxy- and 3 : 4 : 5-trimethoxy-benzoyl chlorides. Phosphorus pentachloride may be used in place of thionyl chloride, but gives poorer yields. o-*Methoxybenzoyl cyanide* crystallises from ligroin in long, yellow needles, m p. 56°, b. p. 161°/12 mm. (Found: C, 67·15; H, 4·2. $C_9H_7O_2N$ requires C, 67·1; H, 4·35%). It is readily soluble in most organic solvents and is rapidly hydrolysed by water.

p-Methoxybenzoyl cyanide has m. p. 63—64°, b. p. 150°/12 mm., and 3 : 4 : 5-trimethoxybenzoyl cyanide, m. p. 136—137° (compare Mauthner, *loc. cit.*). *Cinnamoyl cyanide*, m. p. 114—115°, was made by the acylation of hydrogen cyanide for the first time (compare Claisen and Moritz, *Ber.*, 1880, **13**, 2124).

Preparation of Benzils.—Dry hydrogen chloride was passed

rapidly for 2½ hours into a solution of the acyl cyanide (1 mol.) and resorcinol (or phloroglucinol) (1·1 mols.) in dry ether. *p*-Methoxy- and 3 : 4 : 5-trimethoxy-benzoyl cyanides, which are sparingly soluble in ether, were dissolved in chloroform and added to the ethereal solution of resorcinol (or phloroglucinol). The presence of chloroform hastened the deposition of the ketimine salt. The solution, which in every case turned red, was kept in ice for 3 days. The deposited ketimine hydrochloride was washed with ether, dissolved in just sufficient water, and the solution warmed to 60° and treated with sodium acetate, which precipitated the white, crystalline ketimine. This was readily soluble in dilute hydrochloric and sulphuric acids, the latter solution depositing a crystalline sulphate, generated ammonia when gently warmed with dilute aqueous sodium hydroxide, and was converted into the colourless benzil by boiling aqueous sodium acetate, the golden-brown colour of the solution soon fading to pale yellow. The following changes therefore probably occur during the hydrolysis :



Aqueous solutions of the ketimine hydrochlorides required several hours' warming on the water-bath before hydrolysis was complete.

2 : 4-*Dihydroxybenzil* has m. p. 239°, turning reddish-brown at about 234° (Found : C, 69·8; H, 4·2. $C_{14}H_{10}O_4$ requires C, 69·4; H, 4·1%).

2 : 4-Dihydroxybenzil was described by Finzi (*Monatsh.*, 1905, **26**, 1128) as a brown, amorphous substance, m. p. 239°. We were unable to make the dioxime and repetition of Finzi's experiment for the preparation of its hydrochloride failed to give the result he stated.

2 : 4-*Diacetoxybenzil* was prepared by boiling a solution of the benzil in acetic anhydride for 4 hours and pouring it into water, when the acetyl compound separated as a thick, pasty mass which soon solidified. It crystallised from alcohol in colourless needles, m. p. 159° (Found : C, 66·5; H, 4·4. $C_{18}H_{14}O_6$ requires C, 66·25; H, 4·3%).

The same method was employed for the preparation of the acetyl derivatives of the other benzils.

2 : 4-*Dihydroxy*-2′-*methoxybenzil* has m. p. 223° after darkening at about 210° (Found : C, 66·3; H, 4·5. $C_{15}H_{12}O_5$ requires C, 66·2; H, 4·4%). The *diacetyl* derivative has m. p. 144° (Found : C, 64·4; H, 4·7. $C_{19}H_{16}O_7$ requires C, 64·1; H, 4·5%).

2 : 4-*Dihydroxy*-4′-*methoxybenzil* has m. p. 234° after darkening at about 225° (Found: C, 66·3; H, 4·6%), and the *diacetyl* derivative has m. p. 178·5° (Found: C, 64·3; H, 4·6%).

2 : 4-*Dihydroxy*-3′ : 4′ : 5′-*trimethoxybenzil* has m. p. 257° after turning pink at 175°, yellow at 200°, and darkening at about 245° (Found: C, 61·6; H, 5·0. $C_{17}H_{16}O_7$ requires C, 61·45; H, 4·8%). The *diacetyl* derivative has m. p. 155° (Found: C, 60·3; H, 4·7. $C_{21}H_{20}O_9$ requires C, 60·6; H, 4·8%).

2 : 4 : 6-*Trihydroxybenzil* has m. p. 287° after darkening at about 260° (Found: C, 65·2; H, 4·2. $C_{14}H_{10}O_5$ requires C, 65·1; H, 3·9%). The *triacetyl* derivative has m. p. 248° (Found: C, 62·6; H, 4·4. $C_{20}H_{16}O_8$ requires C, 62·5; H, 4·2%).

2 : 4 : 6-*Trihydroxy*-2′-*methoxybenzil* has m. p. 235° after darkening at about 200° (Found: C, 62·8; H, 4·3. $C_{15}H_{12}O_6$ requires C, 62·5; H, 4·2%). 2 : 4 : 6-*Triacetoxy*-2′-*methoxybenzil* has m. p. 135°.

2 : 4 : 6-*Trihydroxy*-4′-*methoxybenzil* has m. p. 262° after darkening at about 250° (Found: C, 62·7; H, 4·2%). Its *triacetyl* has m. p. 241° (Found: C, 61·0; H, 4·4. $C_{21}H_{18}O_9$ requires C, 60·8; H, 4·3%).

2 : 4 : 6-*Trihydroxy*-3′ : 4′ : 5′-*trimethoxybenzil* has m. p. 187° (Found: C, 58·6; H, 4·8. $C_{17}H_{16}O_8$ requires C, 58·7; H, 4·6%). The *triacetyl* derivative has m. p. 258° (Found: C, 58·1; H, 4·4. $C_{23}H_{22}O_{11}$ requires C, 58·3; H, 4·6%).

The triacetoxybenzils are only moderately soluble in alcohol and were crystallised from alcohol–acetic acid.

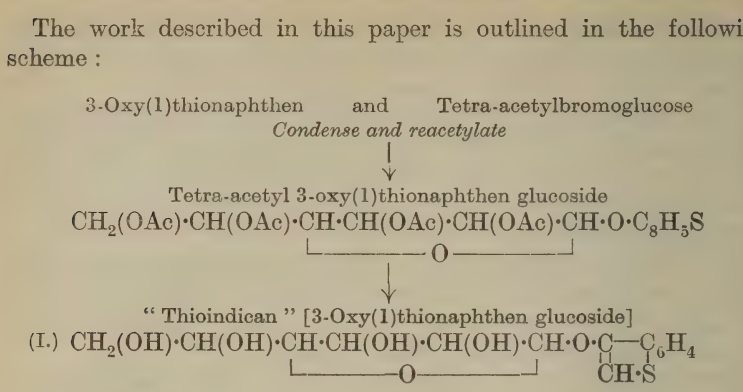
THE UNIVERSITY, MANCHESTER. [*Received, May 1st*, 1925.]

CCXVII.—*Studies of the Glucosides. Part III. The Synthesis of "Thioindican."*

By JAMES CRAIK and ALEXANDER KILLEN MACBETH.

MACBETH and PRYDE (J., 1922, **121**, 1660) deduced the constitution of indican from a study of the hydrolytic products of the methylated glucoside, and hoped to synthesise the glucoside itself through the condensation of tetra-acetylbromoglucose and derivatives of indoxyl. From preliminary attempts it would appear that indoxyl in relatively large amounts is necessary for successful condensation. In view of the difficulty in obtaining sufficient quantities of this material, and of the ease with which it oxidises, it was decided to standardise the experimental methods by examining the conditions in the case of the condensation of tetra-acetylbromoglucose and 3-oxy(1)thionaphthen.

The work described in this paper is outlined in the following scheme:



Experimental.

Tetra-acetylbromoglucose is most conveniently prepared in small quantities by a method devised in the St. Andrews Laboratories. Acetyl bromide (40 g.) is added to anhydrous glucose (10 g.) in a flask immersed in cold water and attached to a reflux condenser. After about 10 minutes a vigorous reaction sets in and the glucose has all dissolved in about ½ hour. The product is poured into ice-water (300 c.c.), and the resulting solid twice washed with sodium bicarbonate solution and then with water until free from acid. The dried ethereal solution of the residue is concentrated greatly, and the addition of light petroleum precipitates an oil which solidifies within 12 hours. Rapid recrystallisation from amyl alcohol gives a pure white, crystalline product which keeps for several months in a desiccator over soda–lime or calcium chloride (yield 10—12 g.).

3-Oxy(1)thionaphthen was prepared by Smiles and McClelland's method (J., 1921, **119**, 1813). We obtained better yields by keeping the temperature at 40—45° during the initial condensation of the 2-thiolbenzoic acid and ethyl acetoacetate and allowing the reaction to continue for about 2 hours.

Condensation of Tetra-acetylbromoglucose and 3-*Oxy*(1)*thionaphthen.*—Attempts to effect the condensation in ethereal solution by shaking with silver oxide gave a product containing a considerable quantity of " thioindigo," from which none of the tetra-acetyl glucoside could be isolated. The best results were obtained by heating tetra-acetylbromoglucose (25 g.) and 3-oxy(1)thionaphthen (13 g.) with quinoline (10 g.) for about 2 hours at 105—110° in an atmosphere of carbon dioxide. The product was poured into ice-water (300 c.c.), extracted with ether, and the extract was washed free from quinoline with *N*-sulphuric acid, then with sodium

bicarbonate solution and water until free from acid. After evaporation of the ether, a rapid steam distillation removed the excess of oxythionaphthen. Thereafter the water was distilled off under reduced pressure, and the dry residual syrup reacetylated by acetic anhydride (60 c.c.) and pyridine (60 c.c.). The crude tetra-acetyl glucoside was obtained by pouring the acetylation mixture into ice-water and ether and washing as described above. The red syrupy residue from the ethereal extract was dissolved in hot alcohol (150 c.c.), and hot water carefully added until turbidity was just appearing. The brown solid obtained on standing yielded in the best experiments about 2·5 g. of white needles, m. p. 106°, of the *tetra-acetyl glucoside* after repeated crystallisation from 60% alcohol. The glucoside is insoluble in water but soluble in the usual organic solvents. In acetone it has $[\alpha]_D + 7{\cdot}4°$ (Found: C, 54·7; H, 4·8; S, 6·7. $C_{22}H_{24}O_{10}S$ requires C, 55·0; H, 5·0; S, 6·7%).

In some experiments, the product obtained was a dark syrup which could not be crystallised even after reacetylation. It contained no bromine, did not reduce Fehling's solution, and analysis showed it to consist essentially of the tetra-acetyl glucoside; and on deacetylation it yielded the parent glucoside.

Deacetylation of the Tetra-acetyl Glucoside.—(a) *With barium hydroxide.* Barium hydroxide (45 c.c. of 0·174 *N*-solution) was added to a hot solution of the tetra-acetyl glucoside (0·8268 g.) in alcohol (40 c.c.). After some minutes barium was precipitated by a stream of carbon dioxide, and the carbonate filtered and washed with alcohol. The united filtrates on evaporation under diminished pressure gave a red syrup, which was extracted with boiling alcohol, and hot water added to the filtrate till turbidity was just appearing. On cooling, "*thioindican*" (I) separated as a mass of fine, glistening needles, coloured pink by traces of "thioindigo." Recrystallised with the aid of a little norit, it gave a pure white product (0·15 g.), m. p. 73·5°, which behaved as a glucoside and did not reduce Fehling's solution until after hydrolysis. It was soluble in alcohol or acetone, and insoluble in ether, light petroleum, or water. The rotation, showing a low dextro-value, was too small at the low concentration available to give a trustworthy reading (Found: C, 53·6; H, 5·3. $C_{14}H_{16}O_6S$ requires C, 53·8; H, 5·1%).

(b) *Alcoholic ammonia.* In this more satisfactory method, the tetra-acetyl glucoside (0·8 g.) was dissolved in a solution of dry ammonia in absolute alcohol. After 10 hours the greater part of the ammonia was removed by a current of air, and the residual solution evaporated under diminished pressure at a bath temperature of 20°. Acetamide was removed by extracting the product

six times with water (10 c.c.), and the residue crystallised as described in (a). Yield 0·13 g. (25% of the theoretical).

Since the red syrup already referred to proved to be essentially glucosidic, it was subjected to hydrolysis as described above. Acetamide and other impurities were removed by repeated extraction with ether. Addition of light petroleum to a concentrated alcoholic solution of the residue precipitated a red solid which on repeated crystallisation from aqueous alcohol yielded fine, white needles of the parent glucoside, m. p. 73·5°.

Estimation of the oxythionaphthen content of the glucoside by simultaneous hydrolysis and condensation with isatin in aqueous hydrochloric acid solution according to the method for estimating indican in plant extracts (Orchardson, Wood, and Bloxam, *J. Soc. Chem. Ind.*, 1907, **26**, 4) gave results which were much too low even when the acid concentration was considerably increased and the time of refluxing greatly extended. The characteristic red condensation product was obtained in a yield of only 48%, the low m. p. of the glucoside and its insolubility in water being doubtless the cause. The estimation may, however, be carried out satisfactorily in alcoholic solution. A solution of "thioindican" (0·0405 g.) in alcohol (100 c.c.) containing isatin (0·23 g.) and concentrated hydrochloric acid (20 c.c.), when boiled under reflux for 10 hours, gave 0·0364 g. of the red condensation product ($C_{16}H_9O_2N_2S$). Theory requires 0·0362 g.

We are indebted to the Department of Scientific and Industrial Research for a grant which enabled one of us (J. C.) to participate in the work.

THE UNIVERSITY, ST. ANDREWS.
THE UNIVERSITY, DURHAM. [*Received, May 14th*, 1925.]

CCXVIII.—*Echitamine.*

By JOHN AUGUSTUS GOODSON and THOMAS ANDERSON HENRY.

THE alkaloid echitamine was first prepared by Gorup-Besanez (*Annalen*, 1875, **176**, 88) from the bark of *Alstonia scholaris*, R.Br. (*Echites scholaris*, L.) and was the subject of much controversy between O. Hesse (*Annalen*, 1875, **176**, 326; **178**, 49 (with Jobst); 1880, **203**, 144; *Ber.*, 1880, **13**, 1841) and Harnack (*Arch. exp. Path. Pharm.*, 1877, **7**, 126; *Ber.*, 1878, **11**, 2004; 1880, **13**, 1648) in the course of which it was shown that Harnack's ditaine (derived from "dita bark," a native name for the bark of *A. scholaris*) is identical with echitamine. Hesse's observations on the alkaloid

were largely confirmed by Bacon (*Philippine J. Sci.*, 1906, **1**, 1007). The position arrived at may be summarised thus: *A. scholaris* bark contains at least two alkaloids: (*a*) ditamine, amorphous, isolated by extracting with ether the residue from an alcoholic extract of the bark, rendered alkaline with ammonia, and (*b*) echitamine (ditaine), obtained by extraction of the same residue, rendered alkaline with solution of sodium or potassium hydroxide, with chloroform, after the removal of ditamine. It is clear from this preliminary work that echitamine is a strong base which, unlike ditamine, cannot be liberated from its salts by ammonia, and the separation of the two alkaloids is based on this fact. The first description of echitamine was given by Hesse (*Annalen*, 1880, **203**, 144), who stated that the free base (echitammonium hydroxide) formed glassy prisms, $C_{22}H_{30}O_5N_2,3H_2O$, m. p. 206°, $[\alpha]_D^{15°} - 28{\cdot}8°$ in alcohol, lost $3H_2O$ at 80° and a fourth molecule of water at 105° in a vacuum, forming a new base, $C_{22}H_{28}O_4N_2$, weaker than the original, but yielding the same hydrochloride, $C_{22}H_{28}O_4N_2,HCl$. Harnack, on the contrary, assigned the formula $C_{22}H_{30}O_4N_2,HCl$ to the hydrochloride.

In addition to *A. scholaris*, several other species of *Alstonia* have been examined. Hesse found in *A. constricta* the amorphous bases porphyrine and chlorogenine (subsequently renamed alstonine) and the crystalline alkaloid, alstonidine (*Annalen*, 1865, Suppl. IV, p. 40; 1880, **205**, 360; *Ber.*, 1878, **11** ,1546. Compare von Muller and Rummel, J., 1879, **35**, 31; Oberlin and Schlagdenhauffen, *J. Pharm.*, 1879, **28**, 576). From a Java species, *A. spectabilis*, R. Brown, Hesse obtained echitamine, ditamine and two other alkaloids, echitenine and alstonamine, the last-named substance being crystalline (*Ber.*, 1878, **11**, 1546; *Annalen*, 1880, **203**, 170), but could find no trace of Scharlec's alstonine (*Genees. Tijd. Ned. Ind.*, 1863, **10**, 209).

Much work has also been done on the sterols and other crystalline, non-nitrogenous substances of Alstonia species. Jobst and Hesse found in *A. scholaris* bark, echikautschin (amorphous); echicerin, $C_{30}H_{48}O_2$, m. p. 157°, $[\alpha]_D + 63{\cdot}75°$; echitin, $C_{32}H_{52}O_2$, m. p. 170°, $[\alpha]_D + 75{\cdot}25°$; echitein, $C_{42}H_{70}O_2$, m. p. 195°, $[\alpha]_D + 85{\cdot}4°$, and echiretin, $C_{35}H_{56}O_2$ (amorphous).

From the dried latex of *Alstonia costulata*, Miq. (*Dyera costulata*, Hook) Sack and Tollens isolated a similar series of sterols (*Ber.*, 1904, **37**, 4110), which Cohen (*Arch. Pharm.*, 1907, **245**, 236) subsequently identified with lupeol, and α- and β-amyrins, and Ultée (*Chem. Weekblad*, 1914, **11**, 456) found the same three constituents in the latex of *A. scholaris*.

The material used in the present investigation consisted of bark

derived from *A. congensis*, Engler. The first sample was collected in the Cameroons by Dr. Lehmann, and for it and the supplies subsequently received from the Cameroons, the Conservator of Forests, Gold Coast, and the Director of Forests, Nigeria, the authors are indebted to the kindness of Dr. Hill, Director of the Royal Botanic Gardens, Kew.

The results of the present investigation confirm Hesse's empirical formula for echitamine, and many of the unexplained points recorded by Hesse and Harnack in the course of their controversy as to the formula of echitamine are accounted for by the fact now established that echitamine is a methyl ester and is hydrolysed with great ease, forming the new base *demethylechitamine*, $C_{21}H_{26}O_4N_2$. It is also shown that echitamine contains a methylimino-group, but whether this has a tertiary or secondary nitrogen is uncertain, as the alkaloid appears to yield a crystalline nitroso-derivative. For the same reason, it is uncertain whether one or two hydroxyl groups are present, as the second acetyl group in the diacetylechitamine now described may indicate the presence of either a hydroxyl group or a secondary nitrogen atom.

Finally, the fact that the parent alkaloid and all the derivatives described give an intense blue colour with Hopkin and Cole's glyoxylic reagent for tryptophan (*Proc. Roy. Soc.*, 1901, **68**, 21) must be taken to mean that echitamine has an indole nucleus, and support for this view is given by the production of an indole-like base, as one product, when echitamine is distilled with alkalis.

A. congensis bark, like other barks of this genus, contains much amorphous alkaloid in addition to echitamine and yields a large quantity of non-nitrogenous products. Of the latter, one substance, a well-crystallised lactone, $C_9H_{14}O_3$, was isolated as a by-product in the purification of echitamine and has been characterised. It is converted by sodium hydroxide into a crystalline sodium salt, $C_9H_{15}O_4Na$, and yields a monoacetyl derivative, so that its formula may be extended thus, $HO\cdot\overline{C_8H_{15}CO\cdot O}$.

For some of the echitamine used in this investigation the authors are indebted to Prof. F. L. Pyman, F.R.S., who isolated it from the bark of another species, *A. Gillettii*, kindly supplied by Fr. Just. Gillet, Curator of the Botanic Gardens, Kisanti, Belgian Congo.

The various Alstonia barks are used in the localities where they occur, as remedies for malaria, but so far no attempt has been made to use echitamine in medicine. The authors are indebted to Dr. J. Trevan of the Wellcome Physiological Research Laboratories for the observation that echitamine hydrochloride is toxic to mice

in doses of 0·3 to 0·5 mg. per 20 g. and that it acts by paralysis of the medulla.

In connexion with the use of the bark in malaria Major Brown of the Wellcome Bureau of Scientific Research found that the hydrochloride was not toxic to protozoa (Glaucoma) at a concentration of 0·03%, but became so at a concentration of 0·0025% in presence of *N*/800-alkali (compare Bacon, *loc. cit.*).

Experimental.

The finely-ground bark (1 kg.) was exhausted with hot alcohol, the concentrated solution poured into warm 1% acetic acid (500 c.c.), and the filtrate from this concentrated to 200 c.c. After agitation with ether (extract A) and chloroform (extract B) in turn to remove wax and other impurities, the liquor was rendered alkaline with sodium hydroxide solution and the liberated alkaloids were dissolved out with chloroform. The residue from the chloroformic solution was dissolved in alcohol, and the liquid rendered slightly acid with hydrochloric acid (10%) and set aside. Echitamine hydrochloride gradually crystallised and was collected, washed with a little alcohol, and recrystallised from water. The yield of crystalline hydrochloride from different samples of *A. congensis* bark varied considerably.

	Gold Coast.	Nigeria.	Cameroons.
Total alkaloid %	0·38 to 0·56	0·11 to 0·12	0·18
Echitamine hydrochloride %	0·18 to 0·34	0·03 to 0·04	0·09

As few data are recorded by previous workers regarding the base and its salts, the opportunity has been taken to characterise these substances.

The hydrochloride obtained was identical with echitamine hydrochloride from *A. scholaris* bark. When crystallised quickly from water, it forms long, anhydrous needles, m. p. 295° (corr.; decomp.), $[\alpha]_D^{15°}$ − 58° (in water; $c = 1\%$) (Found : C, 62·6, 62·9; H, 7·1, 7·1; N, 6·4; Cl, 8·4, 8·5. $C_{22}H_{28}O_4N_2$, HCl requires C, 62·8; H, 6·9; N, 6·9; Cl, 8·4%). When crystallised slowly from water, it forms stumpy prisms, m. p. 292° (corr.; decomp.), $[\alpha]_D^{15°}$ − 54·3° ($c = 1·028$; water) (Found : loss at 100° in a vacuum, 4·79. Calc. for $C_{22}H_{28}O_4N_2,HCl,H_2O : H_2O$, 4·15%). Both forms of the hydrochloride are neutral to litmus. Hesse (*loc. cit.*) records for his hydrochloride $C_{22}H_{28}O_4N_2,HCl$, $[\alpha]_D$ − 57° ($c = 2$; water). The hydrobromide, similarly obtained, forms transparent prisms, m. p. 258° (air-dry; corr.; decomp.), 268° (dry; corr.; decomp.), $[\alpha]_D^{15°}$ − 43·5° for the hydrated salt ($c = 0·804$ in water) (Found : C, 56·4; H, 6·5; Br, 16·9. Calc. for $C_{22}H_{28}O_4N_2,HBr$: C, 56·8; H, 6·3; Br, 17·2%. Loss on drying at 105° in a vacuum, 3·7. Calc. for $C_{22}H_{28}O_4N_2,HBr,H_2O$:

H_2O, 3·7%). Hesse gives the formula $C_{22}H_{28}O_4N_2,HBr,2H_2O$ to his hydrobromide.

The hydriodide, similarly prepared, crystallises from water in long, anhydrous prisms, m. p. 267° (corr.; decomp.) (Found: C, 51·4; H, 5·9; I, 24·0. Calc. for $C_{22}H_{28}O_4N_2,HI$: C, 51·6; H, 5·7; I, 24·8%).

The sulphate is more soluble than the halide salts, separates only after considerable concentration of the neutralised solution, and is best recrystallised by adding alcohol to a strong solution of the salt in water. It forms rosettes of needles, which decompose from 275° onwards; $[\alpha]_D^{15°}$ — 51·6° (c = 2·58 in water) [Found for air-dry salt: loss at 100° in a vacuum, 2·4. $(C_{22}H_{28}O_4N_2)_2,H_2SO_4,H_2O$ requires H_2O, 2·04%. Found in dry salt: H_2SO_4, 11·46. Calc., H_2SO_4, 11·31%].

The *nitrate*, obtained by neutralising the base in chloroform with N/10-nitric acid, separates, on cooling the concentrated aqueous solution, in elongated pyramids, $C_{22}H_{28}O_4N_2,HNO_3,2H_2O$, m. p. 127° (air-dry; corr.; decomp.), 176° (dry; corr.), $[\alpha]_D^{15°}$ — 51·4° (air-dry salt in water; c = 1·01) (Found: loss on drying in a vacuum over sulphuric acid, 8·15. Calc., 7·45%. Found in dry salt: C, 58·9; H, 6·8. Calc., C, 59·0; H, 6·5%).

The neutral oxalate, $(C_{22}H_{28}O_4N_2)_2,H_2C_2O_4$, was only obtained as a gelatinous precipitate, although Hesse (*loc. cit.*) obtained it crystalline (Found: C, 63·9; H, 6·7. Calc., C, 64·3; H, 6·8%). When the calculated quantity of oxalic acid is added to a solution of the base in alcohol, the neutral oxalate first formed dissolves and on adding a little water and removing the alcohol by distillation in a vacuum, rosettes of needles of *echitamine hydrogen oxalate*, $C_{22}H_{28}O_4N_2,H_2C_2O_4,2H_2O$, m. p. 238° (corr.; decomp.), separate on cooling (Found: loss on drying at 100° in a vacuum, 6·3. Calc., H_2O, 7·05%. Found in dry salt: C, 61·0; H, 7·0. Calc., C, 60·7; H, 6·4%).

The picrate is precipitated when picric acid solution is added to the hydrochloride dissolved in water. The air-dry substance softens at 50°, decomposes at 98°, and loses in a vacuum at atmospheric temperature over sulphuric acid 41·3%, corresponding to $24H_2O$. On recrystallisation from dilute alcohol it forms minute rosettes of needles, $C_{22}H_{28}O_4N_2,C_6H_2(OH)(NO_2)_3,2H_2O$, which behave like the air-dry substance on heating (Found: loss on drying in a vacuum over sulphuric acid, 5·5. Calc., 5·6%. Found in dry substance: C, 54·6; H, 5·1. Calc., C, 54·8; H, 5·1%).

Determinations of methoxyl and methylimino-groups by the usual methods on the hydrochloride and hydriodide gave the following results. Hydrochloride: Found; MeO, 7·2; NMe, 7·6. Calc.

for MeO, 7·4; NMe, 6·9%. Hydriodide: Found; MeO, 6·0, 6·1; NMe, 6·0. Calc. for MeO, 6·1; NMe, 5·7%.

Diacetylechitamine Hydrochloride.—Echitamine hydrochloride was mixed with a few drops of pyridine and heated at 100° with six parts by weight of acetic anhydride. On cooling, the diacetyl derivative separated in silky masses of needles and more was obtained by concentrating under reduced pressure. After recrystallisation from ethyl acetate the substance had m. p. 271° (corr.; decomp.) [Found in substance dried at 105° in a vacuum: C, 61·7; H, 6·7; Cl, 6·8; MeO, 6·6; acetic acid (by hydrolysis with phosphoric acid), 26·2. $C_{22}H_{26}O_4N_2Ac_2,HCl$ requires C, 61·8; H, 6·6; Cl, 7·0; MeO, 6·2; acetic acid, 23·8%].

Hydrolysis of Echitamine.—The base used in preparing the salts described above was obtained by dissolving the hydrochloride, as isolated (p. 1643), in water, adding sodium hydroxide, and extracting with chloroform. If complete removal of this solvent by distillation is attempted, the base decomposes as already recorded by Hesse (*Annalen*, 1880, **203**, 144), who called the product oxyechitamine and gave it the formula $C_{22}H_{28}O_5N_2$. The change is probably more profound than Hesse supposed, but the substance has not been examined in the course of this work. The solvent can, however, be largely removed by distillation and the residue, dissolved in alcohol, used for the preparation of salts, but it has not been possible to induce the base to crystallise, though Hesse, as already stated, obtained a base which he at one time regarded as a crystalline tetrahydrate, $C_{22}H_{28}O_4N_2,4H_2O$. In the course of attempts to crystallise the base, water was added (after some days) to a solution in alcohol, prepared as described, and on long standing this deposited crystalline material, more of which was slowly obtained by continued dilution with water.

The same substance was produced more rapidly by heating echitamine hydrochloride in sealed tubes at 120° during 6 hours with 0·24*N*-sodium hydroxide solution (20 c.c. per g. of hydrochloride). It can be recrystallised from hot 70% alcohol and then forms prisms or hexagonal plates, m. p. 290° (air-dry; corr.; decomp.) or 268° (dry; corr.; decomp.). It is sparingly soluble in alcohol, chloroform, or water and is neutral to litmus. It forms a *hydrochloride* crystallising in prisms from hot water, m. p. 306° (corr.; decomp.), which is acid to litmus and much less soluble in water (1 in 209, approx.) than echitamine hydrochloride (1 in 76 approx.) (Found for air-dry base: C, 62·2; H, 7·5; loss in a vacuum at 130°, 8·7. $C_{21}H_{26}O_4N_2,2H_2O$ requires C, 62·0; H, 7·4; H_2O, 8·9%. Found for base dried at 130° in a vacuum: C, 68·0, 68·3; H, 7·3, 7·3; N, 7·8. $C_{21}H_{26}O_4N_2$ requires C, 68·1; H, 7·1; N, 7·6%.

Found for hydrochloride, dried at 100° in a vacuum: C, 62·1, 62·2; H, 6·8, 6·8; Cl, 8·7. Calc. for $C_{21}H_{26}O_4N_2$,HCl: C, 62·0; H, 6·7; Cl, 8·7%).

These analyses indicate that the new base contains $-CH_2$ less than echitamine, and determinations showed that it still contained a methylimino-group but had lost the methoxyl group of echitamine (Found for air-dry base: MeO, 0; NMe, 7·1. $C_{21}H_{26}O_4N_2$ requires NMe, 7·8%. Found for dry hydrochloride: MeO, 0; NMe, 6·8. $C_{21}H_{26}O_4N_2$,HCl requires NMe, 7·1%). The new base is therefore called *demethylechitamine* and all its reactions indicate that the methyl group has been lost from a carbomethoxy-group. This assumption accounts for the neutrality to litmus of demethylechitamine and the acidity to litmus of the hydrochloride, echitamine being strongly alkaline and its hydrochloride neutral to this indicator. The new base, like echitamine and all its salts, gives an intense blue coloration with Hopkin and Cole's glyoxylic reagent for tryptophan.

Action of Nitric Acid on Echitamine.—Harnack stated (*Ber.*, 1878, **11**, 2004) that a carmine-red base was produced by the action of concentrated nitric acid on echitamine, but the substance was not analysed or further described. When nitric acid (18 c.c.) is added to echitamine nitrate (3·19 g.) in water (180 c.c.) and the solution is warmed at 100°, it becomes red, then green, and finally yellow. When sodium hydroxide solution is added to the cooled liquid, a red base is precipitated; and a little more can be recovered by extraction with chloroform. A solution of the red base in dilute alcohol on concentration and standing deposits rosettes of minute needles (yield 1·4 g.), but the bulk of it remains amorphous. After recrystallisation the air-dry base began to decompose at 156° and after drying at 105° in a vacuum showed shrinkage at 163° (corr.) and frothed at 184° (corr.). It is almost insoluble in water, forms a red solution in alcohol and in chloroform a yellow solution with a red fluorescence [Found in air-dry base: loss at 105° in a vacuum, 12·1. $C_{22}H_{26}O_4N_2(NO_2)_2$,$4H_2O$ requires H_2O, 13·2%. Found in base dried at 105° in a vacuum: C, 55·6; H, 6·0; N, 11·6. Calc.: C, 55·7; H, 5·5; N, 11·8%].

The red base still contains intact the methoxyl group of echitamine (Found in dry base: MeO, 6·9. Calc., 6·5%).

The red colour is sharply changed to yellow on neutralisation with acid, and on adding standard alkali to a solution of a known weight of the base in a known excess of standard acid a sharp end-point is reached when a slight permanent red precipitate is formed. A molecular-weight determination by this method gave 474 [Calc. for $C_{22}H_{26}O_4N_2(NO_2)_2$, M, 489]. The red base appears therefore to be a simple dinitro-derivative of echitamine, but the change is

probably more far-reaching than is indicated by the empirical formula.

On treatment with sodium nitrite and dilute hydrochloric acid at 0°, echitamine gives a small yield (8%) of a substance crystallising from ether in rosettes of yellow needles, which shrinks at 140° and melts at 157° (decomp.) and, as it gives Liebermann's reaction, is probably a nitroso-derivative.

Distillation of Echitamine with Alkalis.—When echitamine is heated dry with soda-lime or with an aqueous solution of potassium hydroxide (50%), an alkaline, aqueous distillate is obtained when the temperature is kept below 250°. On neutralisation with hydrochloric acid and redistillation, this affords a distillate which when poured on a hot, oxidised copper spiral yields formaldehyde, due to the presence of methyl alcohol liberated by the hydrolysis of the carbomethoxy-group already referred to (p. 1646). The aqueous liquor in the distillation flask, on evaporation to dryness, left a small quantity of a hydrochloride.

The distillation was continued up to 310° and finally under reduced pressure until nothing more came over. The distillates thus obtained were acidified and extracted with ether, which removed 0·68 g. (from 8·6 g. of alkaloid) of an oil, having a pronounced fæcal odour. This oil gave a red coloration with Ehrlich's reagent, an orange colour with Nelson's solution, and dyed a pine splint, moistened with hydrochloric acid, red. It appeared therefore to be an indole derivative, but no well-defined product could be obtained from it. The acid mother-liquor was rendered alkaline and again extracted with ether, which removed 0·3 g. of a base from which also no crystalline derivatives could be obtained. The alkaline mother-liquor was then distilled, the distillate collected in dilute hydrochloric acid, and the salt produced isolated by the addition of alcohol to the highly concentrated liquor. The crystalline hydrochloride so obtained contained 52·5% of chlorine (Calc. for $CH_3 \cdot NH_2, HCl$: Cl, 52·5%).

The products of this distillation are therefore methyl alcohol, methylamine, an indole derivative, and a third base.

Non-alkaloidal Constituents.

Isolation of a Lactone, $C_9H_{14}O_3$.—No attempt has been made to isolate the components of the waxy and other materials removed in extracts A and B (p. 1642) in the purification of the acetic acid solution, but as these materials retained some alkaloid they were extracted with dilute hydrochloric acid, which was then rendered alkaline with ammonia and re-extracted with chloroform. In this way a crystalline, nitrogen-free product was isolated, more of which

was obtained from the mother-liquors remaining from the separation of crude echitamine hydrochloride. The total yield amounted to 0·02% by weight of the bark used. No evidence has been obtained that this substance is a decomposition product of echitamine. It crystallises from hot water in colourless prisms or long needles, m. p. 74—77° (air-dry; corr.) or 103° (dry; corr.), and has $[\alpha]_D^{15°}$ + 49·9° (air-dry substance in water, $c = 2·5$) or + 56·4° (dry substance in water, $c = 2·5$), is neutral in reaction, fairly soluble in water or chloroform and sparingly soluble in ether (Found: loss on drying in a vacuum at 60° and finally at 90°, 9·84. $C_9H_{14}O_3,H_2O$ requires H_2O, 9·57%. Found in dried substance: C, 63·4, 63·7; H, 8·4, 8·5. $C_9H_{14}O_3$ requires C, 63·5; H, 8·3%).

No methoxyl or dioxymethylene group is present. The substance dissolves in solutions of sodium hydroxide, and the excess of alkali can be titrated back by standard hydrochloric acid with phenolphthalein as indicator. Such determinations indicated that the hydrated substance neutralised 20·7% of sodium hydroxide (Calc., 21·3%) and the dry substance, 23·5% (Calc., 23·5%). A solution in the calculated quantity of sodium hydroxide solution was concentrated, and kept after the addition of dry alcohol, when the corresponding *sodium* salt was obtained as a hygroscopic, crystalline substance (Found: loss on drying at 90—100° in a vacuum, 15·99. Calc. for $2H_2O$, 14·63%. Found in dry salt: Na, 10·64. Calc. for $C_9H_{15}O_4Na$: Na, 10·94%). The substance is therefore a *lactone* of an acid $C_9H_{16}O_4$.

On boiling the lactone with five times its weight of acetic anhydride for 1 hour, concentrating the solution under reduced pressure to half its volume, pouring into water, and extracting with ether we obtained a *monoacetyl* derivative which could not be crystallised (Found for substance dried in a vacuum at 105°: C, 62·5; H, 7·8. $C_9H_{13}O_3Ac$ requires C, 62·2; H, 7·6%). On hydrolysis with alkali and distillation of the resulting liquid, after addition of excess of sulphuric acid, 32·1% of acetic acid was obtained as determined by titration (acetic acid required for $C_9H_{13}O_3Ac$, 28·3%). The residue in the flask, on thorough extraction with chloroform, yielded 79·3% by weight of the original substance used (Calc. for $C_9H_{14}O_3$ from $C_9H_{13}O_3Ac$, 80·2%). The recovered lactone had m. p. 98—100° and $[\alpha]_D^{15°}$ + 55·8° after drying in a vacuum at 100°.

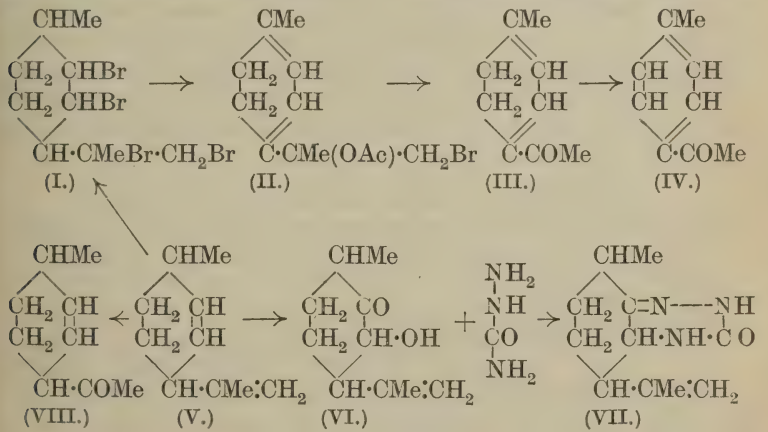
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CCXIX.—*Chenopodium Oil. Part II. The Hydrocarbon Fraction.*

By Thomas Anderson Henry and Humphrey Paget.

The presence of a lævorotatory component in the hydrocarbon fraction of chenopodium oil was first recognised by Kremers (*Pharm. Rev.*, 1907, **25**, 155), and since then numerous efforts have been made to isolate and identify it. Nelson obtained, by bromination of the hydrocarbon fraction, a substance which he regarded as *l*-limonene tetrabromide (*J. Amer. Chem. Soc.*, 1920, **42**, 1204), but on repeating this work the authors found that the product so obtained was optically inactive, differed in crystalline form and physical constants from all the known terpene tetrabromides, and therefore could not be *l*-limonene tetrabromide, but must be derived from a terpene so far unknown. Up to that time only *p*-cymene and α-terpinene had been definitely recognised as present (J., 1921, **119**, 1714).

The authors now show that Nelson's tetrabromide (I) on treatment with silver acetate yields an acetoxybromide (II), which is oxidised by chromic acid to *p*-tolyl methyl ketone (IV), probably through the dihydroketone (III). These reactions are best explained



by the assumption that the tetrabromide is derived from the terpene $\Delta^{2\cdot8(9)}$-*p*-menthadiene (V). Support for this view is obtained from the fact that the total hydrocarbon fraction on treatment with chromic acid is partly oxidised to dimethylacetonylacetone (derived from α-terpinene) and a hydroxy-ketone, $C_{10}H_{16}O_2$ (VI), the semicarbazone of which readily loses water, like other *o*-hydroxy-ketones derived from hydroaromatic substances

(compare Manasse, *Ber.*, 1897, **30**, 668), forming a base, $C_{11}H_{17}ON_3$ (VII). Further, the total hydrocarbon fraction on oxidation by permanganate yields a minute quantity of a substance, $C_9H_{14}O$, which may be tetrahydro-*p*-tolyl methyl ketone (VIII). The substances $C_{10}H_{16}O_2$ and $C_9H_{14}O$ are not obtainable by the separate oxidation of any of the known components (*p*-cymene, α-terpinene, *l*-limonene; see below) of the total hydrocarbon fraction, and it is consequently assumed that they come from the terpene * yielding the tetrabromide.

The same formula has been used already for Tschugaeff's *iso*-limonene (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 988) and Aschan's diprene (*Annalen*, 1924, **439**, 221), neither of which has been fully described, and it is possible that further work may prove all three to be identical, in which case the name *iso*limonene should have priority. It is of interest to note that all three occur along with limonene.

The removal of the readily oxidisable components (α-terpinene and terpene *A*) by partial oxidation of the total hydrocarbon fraction with chromic acid leaves a mixture of *p*-cymene and the lævorotatory component, the identity of which has been a subject of conjecture since 1907. On bromination followed by removal of the *p*-cymene, which inhibits crystallisation, *l*-limonene tetrabromide was isolated in good yield and the presence of *l*-limonene was confirmed by the formation of its characteristic oxidation products, hydroxyterpenylic and lævulic acids. It is also shown that on oxidation by permanganate in acetone, *l*-limonene yields an oily lactone acid, $C_9H_{14}O_5$, derived from a dihydroxy-dicarboxylic acid, $C_9H_{16}O_6$, for which the constitution

$$OH\cdot CHMe\cdot CH_2\cdot CH_2\cdot \overset{*}{C}H[CH(OH)\cdot CO_2H]\cdot CH_2\cdot CO_2H$$

is suggested, since it furnishes lævulic and acetic acids by oxidation with chromic acid, fission taking place at $\overset{*}{C}$. This acid is closely related to two acids,

$$CH_2Ac\cdot CH_2\cdot CHAc\cdot CH_2\cdot CO_2H \longrightarrow CO_2H\cdot CH_2\cdot CH_2\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H,$$

mentioned, without description, by Tiemann and Semmler (*Ber.*, 1895, **28**, 2150) as resulting from the oxidation of limonene erythritol.

In the course of this work large quantities of the total hydrocarbon fraction of chenopodium oil have been worked up, and from the first runnings of these a few c.c. of a substance, which is probably *sym*-dimethylethylene oxide, C_4H_8O, was isolated.

* To save space, and to avoid further additions to the synonymy of terpenes, this component is referred to later as terpene *A*.

The following substances have now been identified as components of chenopodium oil.

p-Cymene.	*sym*-Dimethylethylene oxide (?).	Ascaridole.
α-Terpinene.	Butyric acid.	Ascaridole glycol.
$\Delta^{2,8,9}$ *p*-Menthadiene.	Methyl salicylate.	Ascaridole glycol anhydride.
l-Limonene.	Salicylic acid.	

The chief interest of chenopodium oil lies in its use as an anthelmintic, and it is being employed on a large scale in anti-hookworm campaigns in various parts of the world. Drs. Smillie and Pessôa, who have been engaged in researches on hookworm disease under the auspices of the Brazilian Government and the Rockefeller Foundation in Brazil, have kindly tested pharmacologically and clinically the chief components of chenopodium oil isolated in these laboratories, and their results have been published elsewhere (*J. Pharm. Expt. Ther.*, 1924, **24**, 359). They show that ascaridole, the chief component of the oil, is a remarkably efficient anthelmintic, and that none of the other constituents can be regarded as of value for this purpose.

Experimental.

When a receiver cooled in ice and salt was inserted during the separation of the hydrocarbon fraction from ascaridole by distillation at low pressure, a small amount of a colourless, volatile, pungent-smelling liquid was collected. On redistilling this, a little was obtained at 65—75°/760 mm., the greater part boiling between 120—170°, and consisting chiefly of terpenes and *p*-cymene. After drying over potassium carbonate, the lower-boiling fraction had b. p. 64—78°, $d_{15^\circ}^{15^\circ}$ 0·837, $d_0^{0^\circ}$ 0·8409, $[\alpha]_D^{15^\circ} + 0{\cdot}10^\circ$, $n_D^{20^\circ}$ 1·3968 to 1·3981, *M* (vapour density) 70·2 (Found: C, 66·4; H, 12·4. C_4H_8O requires C, 66·7; H, 11·1%; *M*, 72).

The odour and the characters of this substance indicate that it might be one of the butylene oxides (possibly *sym*-dimethylethylene oxide), b. p. 56—57; $d_0^{0^\circ}$ 0·8344, but, as the figures given above show, the small quantity obtained was still highly impure.

The hydrocarbon fraction distilled between 170° and 185°/760 mm. but all attempts to isolate fractions of constant boiling point failed; considerable separation was, however, effected by repeated slow distillation through a 12-bulb Young dephlegmator. Four litres of the hydrocarbon fraction so treated gave the following results:

Fraction	1	2	3	4	5
B. p.	170—174°	174°	174—175°	175—175·5°	175·5—176°
Amount (g.)	20	40	150	1100	30
α (1-dcm.) ...	−14°	−15°	−16°	−17°	−17·5°
Fraction	6	7	8	9	
B. p.	176—177°	177—178°	178—180°	180—184°	
Amount (g.)	800	800	900	150	
α (1-dcm.) ...	−18°	−19°	−20°	−18·5°	

α-Terpinene nitrosite could be obtained from all these fractions, while only fractions 1 to 4 gave the tetrabromide, m. p. 117°, characteristic of terpene *A*, the best yield being obtained from fraction 1. Fraction 4 was repeatedly redistilled to furnish a little more of fractions 1 to 3, and the residue used with fractions 6, 7, and 8 for the identification of the lævorotatory component. It was shown previously (*loc. cit.*, 1717) that the α-terpinene present in these fractions could be removed by agitation with Beckmann's chromic acid mixture, leaving the lævorotatory terpene mixed with *p*-cymene, and this mixture is referred to later as fraction B. It has the following average characters: b. p. 176·5° to 177°/758 mm., $d_{27.5°}^{23.5°}$ 0·8545, $[\alpha]_D^{15°}$ − 23·08°, $n_D^{20°}$ 1·48637 [Found: C, 89·1, 88·9, 88·8; H, 10·9, 10·6, 10·65%, which corresponds with a mixture of terpenes $C_{10}H_{16}$ (C, 88·2; H, 11·8) and *p*-cymene $C_{10}H_{14}$ (C, 89·6; H, 10·4) in proportion 40 : 60, and 63% of *p*-cymene can be isolated from it by oxidation with permanganate in acetone (see below)]. It yields no terpinene nitrosite, nor any of the oxidation products of α-terpinene, and no terpene *A* tetrabromide could be obtained from it.

Examination of Fraction B.

Bromination.—On bromination by the method already described (*loc. cit.*, p. 1717) a yellow, viscous oil was obtained which, even after standing for several months below 0°, deposited no crystals and gradually changed to a nearly solid tar. If, however, the freshly-brominated product, freed from chloroform and hydrogen bromide by aspiration, was quickly distilled until the bulk of the *p*-cymene was removed at about 105°/10 mm., the residual brown oil, on standing, became filled with leafy crystals, m. p. 104° after recrystallisation from alcohol. A mixture with an equal quantity of *d*-limonene tetrabromide melted at 124° and showed no depression of melting point on further admixture with dipentene tetrabromide. A mixture with the tetrabromide of terpene *A* (m. p. 117°) melted at 90—92°. The substance is therefore *l*-limonene tetrabromide (Found: Br, 69·9; $[\alpha]_D^{19°}$ − 66·12°. *l*-Limonene tetrabromide, $C_{10}H_{16}Br_4$, requires Br, 70·2% and has $[\alpha]_D^{9°}$ − 73·45°).

Oxidation by Permanganate in Acetone.—Fraction B (700 c.c.) mixed with acetone was treated with powdered potassium permanganate (1200 g.) in quantities of 10 g. at a time. The acetone was then distilled off and the residue steam-distilled, yielding 436 c.c. of *p*-cymene (62·3% of the mixture used) having α − 0·7°. The residual alkaline liquor, combined with the washings of the precipitated manganese dioxide, was concentrated to low bulk (compare *loc. cit.*, p. 1719), shaken with ether and ethyl acetate

to remove a small amount of neutral matter, from which traces of the carbonyl compound $C_9H_{14}O$ were isolated (p. 1658), then acidified and again extracted with ether (i), and ethyl acetate (ii). After removal of acetic acid by heating under reduced pressure, these extracts amounted to (i) 61·3 g. and (ii) 15·6 g. and consisted of oily acids, which could not be induced to crystallise either as such or in the form of derivatives. They were therefore converted into ethyl esters, and these distilled under reduced pressure, giving fraction (a), b. p. 117—170°/11 mm., $[\alpha]_D^{20°} - 4{\cdot}8°$; fraction (b), b. p. 170—215°/11 mm., $[\alpha]_D^{20°} - 4{\cdot}8°$, which from the long range of boiling point were obviously mixtures.

After many attempts to isolate a pure acid from these esters it was found that by hydrolysing them with sodium hydroxide in alcohol, a sodium salt, insoluble in alcohol, was produced, which though hygroscopic could be obtained in a granular condition by filtering rapidly from the excess of alcoholic soda, washing thoroughly with 96% alcohol, and drying in a vacuous desiccator. More of this sodium salt was secured by distilling the solvent from the mother-liquors and boiling the residue with dry alcohol. Finally, the viscous residual mixture of soluble sodium salts was dissolved in water, shaken with ether to remove a small amount of neutral tar that had formed, then acidified, and the liberated acid recovered by extraction with ether. This solvent having been distilled off, the acid was boiled with baryta, the excess of the latter removed by carbon dioxide, the filtrate taken to dryness in a vacuum, and the residue boiled with alcohol, which caused the separation of an insoluble barium salt, a little more of which was obtained by repeating the process. Finally, there was left a comparatively small amount of a mixture of barium salts soluble in alcohol, from which a little more material could be separated by precipitation as the thorium salt, but this method was not pursued further. The insoluble sodium and barium salts, isolated as described above, were purified as far as possible by repeated boiling with 96% alcohol, and then gave the following results on analysis, which showed them to be salts of the same acid. *Sodium* salt. Found: Na, 17·0%. *Barium* salt, Found: Ba, 39·1%. Calc. for $C_9H_{14}O_6Na_2$, Na, 17·4%; calc. for $C_9H_{14}O_6Ba$, Ba, 38·6%. The free acid, regenerated from either the sodium or barium salt, boiled at about 210°/34 mm. and formed a colourless, viscid oil (Found: C, 54·0, 53·9; H, 6·4, 6·8. $C_9H_{14}O_5$ requires C, 53·5; H, 6·9%).

On direct titration with *N*-soda solution no definite end-point could be obtained, but when the acid was boiled with excess of *N*-soda for at least 30 minutes and the excess of alkali titrated

back with *N*-acid satisfactory end-points were reached and the amount of soda used was equivalent on the average to sodium (Na) 22·19%. For conversion of $C_9H_{14}O_5$ into $C_9H_{14}O_6Na_2$ the amount of sodium (Na) required is 22·7%.

The silver salt of the acid is relatively stable at atmospheric temperatures even on exposure to light; it dissolves in boiling water and if the solution is filtered rapidly from the small amount of reduced silver formed, re-deposits the salt on cooling as a colourless granular powder, which, however, cannot be dried for analysis without the application of heat, which leads to reduction; and the results are always from 2 to 4% high in silver. Small amounts of the barium salt have been obtained in crystalline form by the cautious addition of alcohol to a 25% solution of the salt in water, but the crystals are very deliquescent, and it was not found practicable to secure enough crystallised barium salt for examination in this way.

The acid gave no derivative with semicarbazide, hydroxylamine, or phenylhydrazine.

To a solution of 2·6 g. of the sodium salt in 30 c.c. of water 30 c.c. of Beckmann's chromic acid mixture were added and the mixture was left standing with occasional agitation for 4 days. It was then thoroughly extracted with ether, which removed 1·52 g. of oily acids, smelling strongly of acetic acid. This residue was left in a vacuum over caustic potash until the bulk of the acetic acid was removed, and then treated with solution of semicarbazide in alcohol, when in the course of a few hours it deposited a copious crop of crystals of a semicarbazone, m. p. 182°; after recrystallisation from alcohol, this rose to 194° (corr.) and showed no change on further crystallisation and no depression when mixed with lævulic acid semicarbazone. The oxidation products of the $C_9H_{14}O_5$ acid are therefore lævulic and acetic acids, and in view of this and the results recorded above the authors regard this acid as a lactone of the acid $OH{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH[CH(OH){\cdot}CO_2H]{\cdot}CH_2{\cdot}CO_2H$ (p. 1650).

The acids regenerated from the barium salts soluble in alcohol referred to above also yield lævulic and acetic acids on oxidation with chromic acid and therefore probably still contain some of the $C_9H_{14}O_5$ lactone acid, which seems to be the principal product of the oxidation of limonene by permanganate in acetone solution.

Oxidation by Permanganate in Water.—Fraction B (100 c.c.) was added in four portions to 1 litre of water containing 94 g. of potassium permanganate, and shaken occasionally till decolorised. The mixture was then steam-distilled to remove unchanged hydrocarbon, and the residual liquor in the distillation flask, with the washings from the precipitated manganese dioxide, thoroughly

extracted with ether, yielding a little cuminaldehyde (derived from *p*-cymene), which was identified by a mixed melting point determination of the semicarbazone (m. p. 210°). The liquor was then concentrated to low bulk, made acid, and shaken with (i) ether and (ii) ethyl acetate. The ethereal extract after removal of the solvent was distilled under reduced pressure, and yielded two fractions, the first a thick oil and the second crystalline, m. p. 159—160°, and consisting of *iso*propenylbenzoic acid, formed by distillation of hydroxy*iso*propylbenzoic acid, which is known as an oxidation product of *p*-cymene under these conditions (Found : C, 73·6; H, 6·4. Calc. for $C_{10}H_{10}O_2$: C, 74·1; H, 6·2%. Found in silver salt : Ag, 40·9. Calc. for $C_{10}H_9O_2Ag$: Ag, 40·15%). The oily fraction gave a semicarbazone, which after recrystallisation melted constantly at 194° and showed no depression of melting point when mixed with lævulic acid semicarbazone (Found : C, 41·9; H, 6·7. Calc. for $C_6H_{11}O_3N_3$: C, 41·6; H, 6·3%). The ethyl acetate extract, on removal of the solvent, deposited a crystalline acid, m. p. 195° (Found : C, 50·2; H, 6·4. $C_8H_{12}O_5$ requires C, 50·85; H, 6·4%). The substance remained unchanged in m. p. after recrystallisation from boiling alcohol and produced no depression when mixed with hydroxyterpenylic acid, $C_8H_{12}O_5$, already known as an oxidation product of *d*-limonene (Godlewski, *J. Russ. Chem. Soc.*, 1899, **31**, 211).

As lævulic acid has not been previously mentioned as formed in the oxidation of limonene by permanganate in water, commercial limonene was oxidised as described above, and yielded hydroxyterpenylic and lævulic acids, but no cuminaldehyde or *iso*propenylbenzoic acid.

From the foregoing results it is clear that fraction B of the chenopodium oil hydrocarbons contains, in addition to *p*-cymene, *l*-limonene.

Nature of Terpene A.

As already stated, it has not been possible to isolate this terpene, or to obtain mixtures containing more than 10 to 12% of it as indicated by the amount of tetrabromide obtainable. For evidence of its constitution reliance has therefore had to be placed on (i) reactions of the only crystalline derivative, the tetrabromide, and (ii) the formation of certain substances when mixtures containing it are oxidised.

Oxidation of the Total Hydrocarbon Fraction by Chromic Acid.—The total hydrocarbon fraction of chenopodium oil was oxidised as already described (*loc. cit.*, p. 1717). After separation by steam distillation of the unattacked hydrocarbons (2150 c.c. from 2500 c.c.) there remained in the distillation flask 70 g. (about 1·5%) of a thick

oil, which, after drying, was distilled under reduced pressure, yielding an oil, b. p. 138—154°/19 mm., and a hard, pitch-like residue, which decomposed on further heating. The oil, after standing in solution in ether over potassium carbonate, was redistilled in two fractions, b. p. 110—120°/15 mm. and 120—136°/15 mm. Both were pale yellow, viscous oils having a faint carvone-like odour; they yielded no solid derivatives with phenylcarbimide or *p*-nitrobenzoyl chloride, but on addition of semicarbazide in aqueous acetic acid solution were converted in the course of 3 days into semi-solid masses, which, when rubbed with alcohol, became crystalline, m. p. 140° (air-dry) and 194° when completely dried at 100°; after recrystallisation from boiling alcohol, they melted at 157° (air-dry) or 204° (dried at 120° in a vacuum), and these melting points were unchanged after a further crystallisation from alcohol. The acetic acid of crystallisation (see below) persists when the air-dry substance is crystallised from boiling alcohol, but if the dried substance is recrystallised from alcohol or boiling water the product obtained melts at 204° and is anhydrous. From all solvents the substance forms rosettes of transparent prisms [Found: loss on drying at 120° in a vacuum, 21·2%. $C_{11}H_{19}O_2N_3,C_2H_4O_2$ requires loss (acetic acid), 21·05%. Found in dried material: C, 58·6, 58·7; H, 8·6, 8·4; N, 19·2. $C_{11}H_{19}O_2N_3$ requires C, 58·6; H, 8·5; N, 18·6%]. The substance is therefore a *semicarbazone* of a product, $C_{10}H_{16}O_2$, probably a *keto-alcohol*. When the semicarbazone is formed in presence of alcohol and acetic acid, or when it is repeatedly boiled with water, there is formed a *base* which has only been isolated as the *acetate*, minute rosettes of needles, m. p. 206°, from water by slow evaporation, and the *picrate*, brilliant yellow needles, m. p. 158°, from acetone or acetone and benzene. This differs from the semicarbazone by the elements of a molecule of water [Found (i) in acetate: C, 57·5, 58·2; H, 8·3, 8·1. $C_{11}H_{17}ON_3,C_2H_4O_2$ requires C, 58·05; H, 7·8%. Found (ii) in picrate: N, 18·6. $C_{11}H_{17}ON_3,C_6H_2(NO_2)_3\cdot OH$ requires N, 19·3%].

It is clear from this that the semicarbazone readily undergoes internal condensation, losing a molecule of water, and on this account it is regarded as having the constitution represented by formula (VI), and the base $C_{11}H_{17}ON_3$ formed from it as having formula (VII).

Only part of the oil reacts with semicarbazide solution and after the whole of the semicarbazone has been separated the mother-liquor on dilution with water yields a thick oil, which can be extracted with ether. This could not be induced to crystallise, nor could it be distilled without some decomposition. It appears,

however, to be a derivative of α-terpinene, since on oxidation with aqueous permanganate it gave a good yield of the mixed *anti*- and *para*-forms of αδ-dihydroxy-α-methyl-δ-*iso*propyladipic acid, m. p. 189°, and showed no depression of melting point on addition of a recrystallised mixture in equal parts of these two forms of this acid (J., 1923, **123**, 1878).

In this oxidation by Beckmann's mixture, α-terpinene is converted into dimethylacetonylacetone, the yield being about 3% of the total hydrocarbon fraction taken. The substance was identified by conversion into the semicarbazide derivative, which melted at 201° and showed no depression of melting point when mixed with the semicarbazide derivative prepared from synthetic dimethylacetonylacetone (Found: C, 59·2; H, 8·9; N, 23·05. Calc. for $C_9H_{15}ON_3$: C, 59·7; H, 8·3; N, 23·2%). Some *p*-tolyl methyl ketone was also formed in the oxidation, and was identified by means of its semicarbazone (Found: C, 62·1; H, 6·6. Calc., C, 62·8; H, 6·8%), m. p. 210°, which showed no depression when the substance was mixed with *p*-tolyl methyl ketone semicarbazone. α-Terpinene, *d*-limonene, and *p*-cymene have all been treated separately with Beckmann's mixture, and their oxidation products are being examined, but none of them yields the substance $C_{10}H_{16}O_2$ described above, and it seems safe to assume that this is derived from terpene *A*.

Oxidation of the Total Hydrocarbon Fraction by Permanganate in Acetone.—When the total hydrocarbon fraction is oxidised by permanganate in acetone, the principal products are a mixture of the *para*- and *anti*-forms of αδ-dihydroxy-α-methyl-δ-*iso*propyladipic acids already described by the authors (J., 1923, **123**, 1878) and dimethylacetonylacetone, resulting from the further oxidation of these acids derived from α-terpinene, *p*-tolyl methyl ketone, and a little cuminic acid, both arising from *p*-cymene, and a mixture of optically active oily acids identical with those, described above (p. 1653), derived from *l*-limonene. The only other product was obtained by extracting the concentrated neutral aqueous liquors with ether, which removed a viscous, brown oil too small in amount to permit of direct purification. From this a crystalline semicarbazone was obtained, which on recrystallisation from boiling alcohol formed colourless needles, m. p. 204° (corr.), which became yellow on exposure to light (Found: C, 61·3, 61·5; H, 8·7, 8·15; N, 21·3. $C_{10}H_{17}ON_3$ requires C, 61·5; H, 8·7; N, 21·5%). On hydrolysis, the semicarbazone furnishes an oil smelling like a mixture of menthone and cuminaldehyde, and from this oil the semicarbazone cannot be regenerated. This semicarbazone is optically inactive, and, if it comes from terpene *A*, should be

that of Δ^2-tetrahydro-*p*-tolyl methyl ketone, $C_9H_{14}O$ (VIII), but as the yield of semicarbazone obtained only amounts to 0·24% of the total hydrocarbon fraction used, it has not been possible to accumulate enough for examination in detail.

Tetrabromide of Terpene A.—The preparation and isolation of the tetrabromide has been described already (*loc. cit.*, p. 1717). Of numerous attempts to use this tetrabromide as a means of gaining information regarding the constitution of terpene *A*, only the following have given useful results. 12·5 G. of the tetrabromide were added to a solution of 1·9 g. of sodium in methyl alcohol, and the mixture, after boiling for 7 hours, was steam-distilled, when 4·4 g. of a heavy, colourless oil were obtained, b. p. 115—120°/18 mm., containing 30·2% of bromine ($C_{10}H_{14}Br{\cdot}OMe$ requires Br, 32·6%). This appeared to be a monobromomethyl ether corresponding to the monobromomethyl ether which Wallach obtained from limonene tetrabromide (*Annalen*, 1894, **281**, 127). The removal of the fourth bromine atom by the further use of sodium converted the monobromomethyl ether almost wholly into *p*-cymene. Unlike Wallach's product, it did not after reduction yield a menthenone by oxidation with either chromic acid or permanganate. It was only slowly attacked by either agent, and the products in both cases were *p*-tolyl methyl ketone with a little *p*-toluic acid. In further experiments, silver acetate was used: 5·3 g. of the tetrabromide were shaken with 5·8 g. of silver acetate in 10 c.c. of acetic acid during 8 hours, then made alkaline with sodium carbonate, and shaken with ether, which removed a yellow, viscous oil (3·1 g.). This on solution in light petroleum (b. p. 40—60°) deposited some insoluble tar, and the oil thus purified, after drying over potassium carbonate and removal of the petroleum by distillation and exposure in a vacuum until of constant weight, gave the following results: C, 52·8; H, 6·1; Br, 29·2 ($C_{10}H_{14}Br{\cdot}O{\cdot}CO{\cdot}CH_3$ requires C, 52·6; H, 6·2; Br, 29·3%). The substance is therefore a *bromoacetoxydihydro*-p-*cymene* (II) and this was confirmed by hydrolysing a weighed quantity (0·2175 g.) of the substance in the cold with a known amount of potassium hydroxide in alcohol (30·6 c.c. of *N*/10-KHO), the mixture being allowed to stand for a week, after which the excess of alkali (16·42 c.c. of *N*/10-KHO) was determined by titration with standard nitric acid. The amount of alkali used (14·2 c.c of *N*/10-KHO), after correction for a small amount of bromide (equal to 0·0478 g. Br) formed, was 21·1%, whilst that required for the removal of one acetyl group from $C_{10}H_{14}Br{\cdot}O{\cdot}CO{\cdot}CH_3$ is 20·5%.

Seven g. of the bromoacetoxy-compound were agitated with 30 c.c. of water to form an emulsion; to this 130 c.c. of Beckmann's

chromic acid mixture were added in three portions at intervals of 1 hour, and the whole was shaken for 8 hours. This was extracted with (1) light petroleum, b. p. 40—60°, and (2) ether, and the extracts were dried over anhydrous sodium sulphate. The petroleum extract (1) left an oily residue (2·9 g.) which was pungent, and had an odour of *p*-tolyl methyl ketone; on treatment with semicarbazide it yielded a semicarbazone which after crystallising twice from boiling alcohol formed colourless, opaque prisms melting constantly at 210° and showing a slight rise in melting point to 211° when mixed with an equal quantity of *p*-tolyl methyl ketone semicarbazone prepared from synthetic material. The mother-liquor from the preparation of the semicarbazone was made alkaline with sodium carbonate and shaken with light petroleum, when it yielded 1·7 g. of an oil containing bromine and apparently consisting largely of unchanged material. The ether extract (2) yielded on re-extraction with sodium carbonate solution and acidification of this (*a*) terephthalic acid, colourless crystals, subliming without melting above 280°, and (*b*) *p*-toluic acid, m. p. 177°, showing no depression when mixed with a pure specimen of *p*-toluic acid.

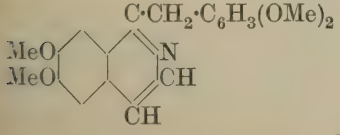
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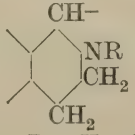
CCXX.—iso*Quinoline Derivatives. Part IX. Preparation and Reduction of* iso*Quinoline and its Derivatives.*

By ROBERT FORSYTH, CHARLES IGNATIUS KELLY, and FRANK LEE PYMAN.

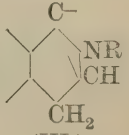
THE reduction of papaverine (I) and *N*-methylpapaverinium salts by means of tin and hydrochloric acid yields not only the expected tetrahydro-derivatives (II), but also, as by-products, the 2 : 4-dihydro-derivatives, pavine and *N*-methylpavine, containing the unique dicyclic system (III) (Pyman, J., 1915, **107**, 176, where earlier references are given). The present inquiry had the object



(I.)



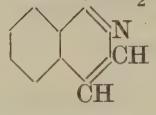
(II.) (R = H or Me)



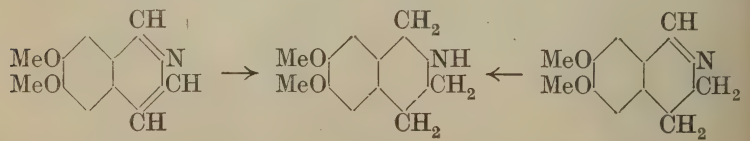
(III.)

of determining whether the formation of by-products of this type on the reduction of *iso*quinoline, by means of tin and hydrochloric acid, is a general property or not, and necessitated a quantitative study of the reduction of pure materials, for the quantities of these by-products to be expected were only small. Thus, the yields of pavine isolated by different investigators range from 8 to about 25% (Pope and Gibson, J., 1910, **97**, 2207), whilst the yield of *N*-methylpavine was 3% of the theoretical.

The reduction of *iso*quinoline itself was first examined, for uncharacterised by-products of its reduction to tetrahydro*iso*quinoline have been noticed by former investigators, and it was uncertain whether these were of the pavine type or due to impurities in the initial material. Experiments showed that pure *iso*quinoline can be reduced to tetrahydro*iso*quinoline in nearly theoretical (96%) yield. The effect of a 1-benzyl group was next studied, and here 1-benzyl*iso*quinoline methiodide gave 1-benzyl-2-methyltetrahydro*iso*quinoline in a yield of 85% of the theoretical, unaccompanied by any other organic base, the deficit being due to partial decomposition of the material with the formation of ammonia. Similarly, the only product isolated after reduction of 1-benzyl-*iso*quinoline (IV) was 1-*benzyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline* (V). The constitution of this substance was proved by its conversion into 1-benzyl-2-methyltetrahydro*iso*quinoline on methylation.

(IV.)  (V.)

The effect of methoxy-substituents in the *iso*quinoline nucleus was next examined, and here also a negative result was obtained, for 6 : 7-dimethoxy*iso*quinoline (VI) gave 6 : 7-*dimethoxy*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline* (VII) in a yield of 94% of the theoretical. The identity of the product was established by comparison with the product of reduction of 6 : 7-dimethoxy-3 : 4-dihydro*iso*quinoline (VIII) (Pyman, J., 1909, **95**, 1610). Similarly, the reduction of 6 : 7-*dimethoxy*iso*quinoline methiodide* gave as the sole isolable product 6 : 7-dimethoxy-2-methyltetrahydro*iso*quinoline (Pyman, J., 1909, **95**, 1266).



(VI.) (VII.) (VIII.)

It has thus been shown that neither a 1-benzyl nor 6 : 7-dimethoxy-groups suffice to induce formation of compounds of the pavine type on the reduction of derivatives of *iso*quinoline, and the further investigation of this problem, which is contemplated, will necessitate the preparation and reduction of 1-benzyl-6 : 7-dimethoxy*iso*-quinoline and possibly also of 1-veratryl*iso*quinoline.

Of the *iso*quinoline derivatives required for this work, a part of the *iso*quinoline itself was isolated from coal tar by fractionation and crystallisation of the acid sulphate as described below, the yield being better than that obtained by Harris and Pope (J., 1922, **121**, 1029), using another method. Several methods for the preparation of 1-benzyl*iso*quinoline were examined, and of these the only satisfactory one was that of Decker and Pschorr (*Ber.*, 1904, **37**, 3397) by the action of benzyl magnesium chloride on *N*-methyl*iso*quinolone and distillation of the 1-benzyl*iso*quinoline methiodide produced. The oxidation of 1-benzyl-3 : 4-dihydro-*iso*quinoline (Pictet and Kay, *Ber.*, 1909, **42**, 1973) gave only 3% of 1-benzyl*iso*quinoline, and the dehydration of α-hydroxy-β-phenyl-acetylamino-α-phenylethane (A) by phosphorus pentoxide gave only 4% of 1-benzyl*iso*quinoline. This last result is in accord with the work of Robinson (J., 1909, **95**, 2167), who obtained only a trace of a picrate, suspected of being 1-benzyl*iso*quinoline picrate, in this way, and is at variance with the results of Pictet and Gams (*Ber.*, 1910, **43**, 2386), who obtained a 40% yield. The latter authors, like Robinson, prepared the carbinol (A) by the reduction of ω-phenylacetylaminoacetophenone, but found it to melt at 123°, whereas Robinson found the m. p. 99°. Here, again, our results confirm those of Robinson, the carbinol (A) proving to melt at 99° whether prepared by Robinson's method or by the action of phenyl-acetyl chloride upon β-hydroxy-β-phenylethylamine.

The preparation of 6 : 7-dimethoxy*iso*quinoline was effected essentially by the method of Rügheimer and Schön (*Ber.*, 1909, **42**, 2374), that is, by the action of sulphuric and arsenic acids upon veratrylaminoacetal, but the technique has been improved. Veratrylaminoacetal was prepared by the reduction of *veratrylidene-aminoacetal*, a more convenient method than the action of chloro-acetal upon veratrylamine, the method of the previous authors (*Ber.*, 1908, **41**, 17).

Experimental.

Preparation of iso*Quinoline.*—Three gallons of "crude pyridine bases" (corresponding to 6 tons of coal tar) were dehydrated by shaking three times with aqueous sodium hydroxide (80° Tw.), and the product (10·85 litres) was distilled up to 170° and then fractionated through a 12-pear column. The various fractions,

b. p. 200—280°, were fractionated similarly twice more, when 2·3 litres (2470 g.) of "heavy quinoline bases," b. p. 230—255°, were obtained. This fraction was converted into acid sulphate, and crystallised fractionally from alcohol, when 185 g. of pure *iso*quinoline hydrogen sulphate, m. p. 207·5° (corr.), were obtained. This gave 102 g. of the base, b. p. 242° (corr.) over a range of 0·5°; m. p. 24° (corr.). The yield of *iso*quinoline from the "heavy quinoline bases" is thus about 4%, whereas Harris and Pope (who refer to previous work on the subject, J., 1922, **121**, 1029) obtained only 1·5% by a more laborious method.

Reduction of iso*Quinoline.*—*iso*Quinoline (6·45 g.), alcohol (68 c.c.), hydrochloric acid (100 c.c. conc.), and granulated tin (42 g.) were heated on the water-bath under reflux for 12 hours. After cooling, the separated tin salts were collected (mother-liquor M) and deprived of tin by means of hydrogen sulphide, when, on evaporation, crude tetrahydro*iso*quinoline hydrochloride (8·0 g.; m. p. 195°) was obtained. It was mixed with aqueous sodium hydroxide and distilled into hydrochloric acid, and the distillate gave, on evaporation, pure tetrahydro*iso*quinoline hydrochloride (7·83 g.; m. p. 196—197°. Hoogewerf and van Dorp, *Rec. trav. chim.*, 1885, **4**, 125, give m. p. 195—197°). The residue from the steam-distillation was extracted with chloroform, which removed a base giving a crystalline hydrochloride, the total residue as hydrochloride, m. p. 280—290°, amounting to only 0·05 g. The mother-liquor M gave, after removal of tin, crude tetrahydro*iso*quinoline hydrochloride (0·3 g.; m. p. 190°; m. p. of mixture with the pure salt, 192°). The total yield of tetrahydro*iso*quinoline is thus 96·35% of the theoretical. To establish its purity, 8·0 g. were mixed with carbon disulphide in dry ether, and the precipitated tetrahydro*iso*quinoline tetrahydro*iso*quinolyldithiocarbamate (Bamberger and Dieckmann, *Ber.*, 1893, **26**, 1208) was decomposed with hydrochloric acid, when 7·86 g. of tetrahydro*iso*quinoline hydrochloride of unchanged m. p. were recovered.

1-*Benzyl*iso*quinoline.*—*A.* After Decker and Pschorr (*Ber.*, 1904, **37**, 3397). Five g. of 1-benzyl*iso*quinoline methiodide (from *N*-methyl*iso*quinolone and benzyl magnesium chloride; yield 36% of pure salt, m. p. 248° [corr.]) were heated under 20—30 mm. until all methyl iodide was removed; the residue then distilled at 222° (corr.)/18 mm. Decker and Pschorr give 211—213°/11 mm. The distillate, which crystallised and melted at 55—56° (corr.), was converted into the hydrochloride, and more of this salt was recovered from the distillation residue (yield 3·5 g. = 86%). This salt crystallises from water in colourless, elongated prisms, which contain $2H_2O$ and melt below 100°, but after drying first in a vacuum

and then at 100°, the substance melts at 185—187° (corr.). Decker and Pschorr give m. p. 171—172°; Pictet and Gams, 175° (Found: H_2O, 12·0. Calc. for $2H_2O$, 12·4%. Found, in dried salt: Cl, 13·9. Calc., Cl, 13·9%). The picrate melted at 184° (corr.). Decker and Pschorr give 184—185° (corr.).

B. After Pictet and Kay (*Ber.*, 1909, **42**, 1973). To 1-benzyl-3 : 4-dihydro*iso*quinoline (2 g.; b. p. 196—197°/12 mm.) in glacial acetic acid (100 c.c.) at 100°, potassium permanganate (1 g.) in water (200 c.c.) was added with shaking in 1½ hours, and the mixture was heated for another hour. After basifying, ether removed an oil (0·8 g.) which was converted into the picrate and crystallised fractionally from alcohol, when 0·11 g. of the nearly pure salt was obtained (yield 3%; m. p. 181—182° [corr.]; not depressed after mixture with an authentic specimen). Numerous attempts to improve upon this yield by varying the conditions were unsuccessful. Pictet and Kay do not state their yield, but indicate that it was poor.

C. After Robinson (J., 1909, **95**, 2167) and Pictet and Gams (*Ber.*, 1910, **43**, 2386). ω-Phenylacetylaminoacetophenone (from phenylacetyl chloride, ω-aminoacetophenone hydrochloride, and sodium hydroxide; yield 50%; m. p. 103°) was reduced by Robinson's method and gave α-hydroxy-β-phenylacetylamino-α-phenylethane (yield 73%; m. p. 99° as stated by Robinson). On attempting the reduction under the conditions employed by Pictet and Gams, a poor yield of a crude product, m. p. 73°, was obtained. α-Hydroxy-β-phenylacetylamino-α-phenylethane was also prepared by mixing 2 g. of β-hydroxy-β-phenylethylamine carbonate (Wolfheim, *Ber.*, 1914, **47**, 1440) with phenylacetyl chloride (2·5 g.) and 20% aqueous sodium hydroxide (15 c.c.), and after purification melted at 99°, alone or mixed with the substance made by Robinson's method.

α-Hydroxy-β-phenylacetylamino-α-phenylethane (40 g.; m. p. 99°) in xylene (200 c.c.) was dehydrated by phosphorus pentoxide (200 g.), and the basic products were collected as described by Pictet and Gams, and converted into the hydrochloride, when 1-benzyl*iso*quinoline hydrochloride (1·8 g.; m. p. [dry] 185°; yield 3·9%) was obtained. A specimen of the picrate prepared from this salt had m. p. 184° (corr.), alone or mixed with an authentic specimen.

Reduction of 1-*Benzyl*iso*quinoline.*—1-Benzyl*iso*quinoline hydrochloride (4·0 g.; air-dried), alcohol (20 c.c.), concentrated hydrochloric acid (20 + 10 c.c.) * and tin-foil (10 + 2·5 g.) were digested

* In this and the following reductions additional quantities of hydrochloric acid and tin were added after some hours.

for 21 hours on the water-bath. Water was added, tin removed, and the solution concentrated and mixed with sodium iodide, when pure 1-benzyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline hydriodide (3·75 g.; anhydrous, m. p. 167—168°) separated. The filtrate was mixed with sodium hydroxide and extracted with ether, 0·2 g. of brown oil being obtained. This was not wholly basic, but gave a turbid solution with hydrochloric acid. After filtration through charcoal and addition of sodium iodide, 0·22 g. of the above iodide, m. p. (crude) 145—155° (not depressed by mixture with the pure salt), was deposited, which after crystallisation from water gave 0·15 g., m. p. 162—165°. The total yield is thus 81% of the theoretical.

1-*Benzyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline hydriodide*, colourless well-formed prisms from water, has m. p. (substance dried at 100°) 167—168·5° (corr.). It is sparingly soluble in cold water (Found : loss at 100°, 5·0. $C_{16}H_{17}N,HI,H_2O$ requires H_2O, 4·9%. Found, in dried salt : C, 54·8; H, 5·1; I, 36·3. $C_{16}H_{17}N,HI$ requires C, 54·7; H, 5·1; I, 36·2%). The *base* (V) was a colourless, viscous oil, which did not crystallise after keeping for 2 days over sulphuric acid in a vacuum. The *picrate* crystallised from alcohol in deep yellow, prismatic needles, m. p. 166—167° (corr.) after drying at 100°.

Methylation.—1-Benzyltetrahydro*iso*quinoline and methyl iodide were heated for a few minutes under reflux, and after removal of uncombined methyl iodide a gummy product remained, doubtless a mixture of the hydriodides of the secondary and tertiary bases with the methiodide of the latter. The bases regenerated from this by means of sodium hydroxide and ether were crystallised fractionally as picrates, when 1-benzyl-2-methyltetrahydro*iso*quinoline picrate separated first. It had m. p. 165—166° (corr.), alone or mixed with a specimen prepared by the reduction of 1-benzyl*iso*quinoline methiodide, and the hydriodides from the two sources also proved to be identical.

Reduction of 1-*Benzyl*iso*quinoline Methiodide.*—The pure methiodide (10 g.; m. p. 248° [corr.]), alcohol (40 c.c.), hydrochloric acid (40 + 20 c.c. conc.), and tin-foil (20 + 5 g.) were heated on a water-bath under reflux for 24 hours. After distilling the alcohol, water was added, when the bulk of the organic tin salts were deposited (mother-liquor L). The gummy deposit was dissolved in water, and deprived of tin by means of hydrogen sulphide. The filtrate was evaporated under diminished pressure to remove excess of hydrochloric acid, and the residue was dissolved in water and mixed with sodium iodide, when pure 1-benzyl-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline hydriodide (8·33 g.) was deposited. Before

and after crystallisation from alcohol, it melted at 174—175° (corr.), separating from alcohol in prismatic columns as stated by Freund and Bode (*Ber.*, 1909, **42**, 1746), who give m. p. 175—180°. The picrate crystallised from alcohol in rhombic tablets, m. p. 165—166° (corr.), as stated by these authors. The mother-liquor L was deprived of tin, mixed with the filtrate from the above hydriodide, basified with sodium hydroxide, and extracted with ether, which removed an oily base (0·35 g.). This was converted into the hydriodide (0·4 g.; m. p. 166—170°) and crystallised from alcohol, when 0·25 g. of the pure salt was obtained. The total yield of the pure salt is thus 86% of the theoretical. The liquor from which the base was extracted contained ammonia. A similar result was obtained on repetition of this experiment, an 84% yield of the pure hydriodide being obtained.

6 : 7-*Dimethoxy*iso*quinoline*.—Veratraldehyde (52·4 g.) and aminoacetal (42 g.) were heated for several hours on the water-bath, until the water, which soon separated, had evaporated. The crude product, obtained in theoretical yield, had m. p. 53—58°, and after crystallisation from ether gave *veratrylideneaminoacetal* in nearly colourless, very pale yellow, well-formed plates, m p. 61—62° (corr.) (Found: C, 64·1; H, 8·3. $C_{15}H_{23}O_4N$ requires C, 64·0; H, 8·2%).

Crude veratrylideneaminoacetal (50 g.) in absolute alcohol * (0·5 litre) was reduced by the gradual addition of sodium (50 g.) and more alcohol. After water had been added, ether collected nearly pure veratrylaminoacetal, which, after removal of solvents at 100°/15 mm., amounted to 45 g. and was suitable for use in the next operation without distillation.

Veratrylaminoacetal has b. p. 208° (corr.)/15 mm. (Found: C, 63·4; H, 8·8. $C_{15}H_{25}O_4N$ requires C, 63·6; H, 8·8%). Rügheimer and Schön (*Ber.*, 1909, **42**, 2374), who did not analyse the compound, give b. p. 197°/11 mm.

Arsenic pentoxide (5 g.) was dissolved in warm water (1 c.c.), concentrated sulphuric acid (10 c.c.) added, and the whole cooled in a freezing mixture. Crude veratrylaminoacetal (5 g.) was run in a few drops at a time with thorough rubbing to dissolve the viscous product. A homogeneous solution was obtained in about ¼ hour, and was kept for 1 hour at the ordinary temperature, and then heated for 1 hour at 100°. The products from 10 such experiments were diluted with water (100 c.c.) and mixed with sufficient 20% aqueous sodium hydroxide to neutralise the bulk of the acid. After cooling, an amorphous precipitate was removed by filtration,

* Fusel oil (at 130°) cannot be substituted for absolute alcohol in this case.

and the liquor basified with sodium hydroxide and extracted with chloroform. (Distressing emulsions are obtained if the removal of the amorphous precipitate is omitted.) The chloroform residue was mixed with hydrochloric acid, the solution evaporated to dryness, and the residual hydrochloride crystallised several times from alcohol. From the final mother-liquors, the base was regenerated by sodium hydroxide, and extracted with chloroform. The chloroform residue was extracted twice with hot ether, and the extract converted into hydrochloride and crystallised from alcohol. In this way, veratrylaminoacetal (50 g.) gave 8·5 g. of pure 6 : 7-dimethoxy*iso*quinoline hydrochloride (dried at 100°), that is 21% of the theoretical. Rügheimer and Schön describe the yield as "satisfactory." This salt crystallises from alcohol in nearly colourless needles, containing $3H_2O$, which are lost at 100°; when anhydrous, it melts and effervesces at 221° (corr.). Rügheimer and Schön give 208—210° (decomp.). The base separated from ether in large prisms, m. p. 93° (corr.); Rügheimer and Schön give 93—94°.

6 : 7-*Dimethoxy*iso*quinoline methiodide* is formed when the base is mixed with methyl iodide. It is sparingly soluble even in hot alcohol, from which it separates on cooling in pale buff, glistening, anhydrous needles, m. p. *ca.* 256° (decomp.; corr.) (Found : I, 38·3. $C_{12}H_{14}O_2NI$ requires I, 38·4%).

Reduction of 6 : 7-*Dimethoxy*iso*quinoline*.—The pure base (4·8 g., m. p. 93°), alcohol (20 + 5 c.c.), concentrated hydrochloric acid (20 + 20 c.c.), and tin-foil (20 g.) were digested for 30 hours on the water-bath. The product was dissolved in hot water (0·7 litre) and freed from tin by hydrogen sulphide; on concentration, 5·22 g. of pure 6 : 7-dimethoxytetrahydro*iso*quinoline hydrochloride were obtained (in three crops). The mother-liquor was evaporated to dryness and mixed with alcohol, when 0·2 g. of the same salt, m. p. 260° after sintering from 256°, separated; the mother-liquor from this, when evaporated to dryness and mixed with absolute alcohol, deposited a further 0·05 g. (m. p. 242—245°; mixed with the pure salt, m. p. 252—258°). The total yield (5·47 g.) amounts to 94% of the theoretical. The final mother-liquor gave on evaporation to dryness a gummy residue (0·11 g.), from which no crystalline base or salt could be obtained.

6 : 7-*Dimethoxy*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline hydrochloride* crystallises from water in colourless quadrilateral plates, m. p. 262° (corr.). It is readily soluble in cold water, and very readily soluble in hot water, but sparingly soluble in cold alcohol (Found : C, 57·8; H, 7·2. $C_{11}H_{15}O_2N,HCl$ requires C, 57·5; H, 7·0%). The *picrate* crystallised from alcohol in broad, yellow needles, m. p. 202—203°

(corr.). The *base* (VII) crystallised from chloroform in colourless plates, which were easily soluble in chloroform, but sparingly soluble in ether. It readily takes up carbon dioxide from the air, and was not obtained free from carbonate (m. p. 80—130°).

6 : 7-Dimethoxytetrahydro*iso*quinoline was also obtained by the reduction of 6 : 7-dimethoxy-3 : 4-dihydro*iso*quinoline with tin and alcoholic hydrochloric acid. The hydrochloride and picrate from this source had the m. p.'s recorded above, alone or mixed with the corresponding salts from the reduction of 6 : 7-dimethoxy*iso*quinoline.

Reduction of 6 : 7-*Dimethoxy*isoquinoline *Methiodide*.—The pure methiodide (10 g.), alcohol (40 c.c.), concentrated hydrochloric acid (40 + 20 c.c.), and tin-foil (20 + 5 g.) were digested for 18 hours on the water-bath, and the product was deprived of tin by means of hydrogen sulphide. The residue remaining after evaporation of the water was dissolved in water and mixed with picric acid (7 g.) in hot water (300 c.c.), when, on cooling, 10·45 g. of 6 : 7-dimethoxy-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline picrate, m. p. 158° (corr.), separated. The base (0·25 g.) regenerated from the mother-liquors was converted into picrate and gave 0·35 g. of the above salt, m. p. 152—153°. The total yield is thus 82% of the theoretical. The identity of the salt, for which Pyman (*loc. cit.*) gives m. p. 159—160° (corr.), was confirmed by the preparation from it of the hydrochloride, m. p. (dry) 217—218° (corr.), and base, m. p. 83—84° (corr.) (Pyman gives m. p. 216—217° [corr.] and 83—84° [corr.] respectively), and by comparison of the latter with an authentic specimen prepared by the reduction of 6 : 7-dimethoxy-3 : 4-dihydro*iso*quinoline methiodide (mixed m. p. 83—84° [corr.]).

We desire to thank (1) the Council of the Lord Kitchener National Memorial Fund for the grant of a scholarship which has enabled one of us (C. I. K.) to take part in the investigation, (2) Messrs. Brotherton and Co., Ltd., tar distillers, Leeds, for raw materials and facilities for the isolation of *iso*quinoline, (3) Professor R. Robinson, F.R.S., and Mr. H. S. Land, B.Sc.Tech., for gifts of *iso*quinoline, and (4) the Wellcome Chemical Research Laboratories for a specimen of 6 : 7-dimethoxy-3 : 4-dihydro*iso*quinoline.

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CCXXI.—*The Surface Tensions of Aqueous Phenol Solutions. Part II. Activity and Surface Tension.*

By Arthur Kenneth Goard and Eric Keightley Rideal.

The equation of Gibbs determining the surface adsorption of substances in solution ("Equilibrium in Heterogeneous Systems," Scientific Papers, Vol. II) should strictly be written in the form $\Gamma = -d\sigma/d\mu$, where σ = surface tension and $\mu = \mu_0 + RT \log_e a$. Γ is here the excess concentration (positive or negative) of the solute at the surface and a is the mean activity of the solute (compare Lewis and Randall, "Thermodynamics," New York, 1923).

Very little attempt has been made hitherto to apply this equation to actual cases, most workers having dealt with systems in which the activity can be equated approximately to the bulk concentration of the solute. Since it is frequently just in concentrated solutions, where this equality fails to hold, that adsorption phenomena become important, it is highly desirable that the strict form of the Gibbs equation should be more widely adopted. As a simple example of the use of activities, we may take the case of a binary liquid mixture at its critical solution temperature, where a small change in the relative proportions of the components does not affect the surface tension, regardless of the amount of surface adsorption (Lewis and Randall, *op. cit.*, Chap. XXI, Exercise 7). It further follows that in the region of this critical point, unless the adsorption exhibit very sudden and violent changes, the surface tension is largely independent of the relative concentrations of the two components. In Part I of this investigation it was shown that the difference between the surface tensions of the two liquid phases formed by phenol and water was only 0·33 dyne/cm. at 0°, and that this difference diminished continuously up to the critical solution temperature. The surface tensions of the two phases are thus remarkably similar, despite large differences of composition. A generalisation of this kind was stated empirically by Antonov in 1907 (*J. Chim. Phys.*, 1907, **5**, 364); it is now seen to be the natural result of the activity relations displayed by two liquids in the "critical zone."

As an example of the opposite kind, in which the activity of a solute may undergo great alteration without any change of concentration, we may take the "salting out" of organic substances from aqueous solutions by the addition of inorganic salts, *e.g.*, that of phenol by sodium chloride. Various experimenters have shown that the toxicity of phenol in aqueous solution is increased by the addition of salt; their results have been summarised by Lash Miller (*J. Physical Chem.*, 1920, **24**, 562). Berczeller (*Biochem. Z.*,

1914, **66**, 173, 191, 202) showed that this increase was accompanied by a lowering of the surface tension. Miller (*loc. cit.*) suggested that both these phenomena are due to an increase in the chemical potential of the phenol; and Lemon (*J. Physical Chem.*, 1920, **24**, 570) and Laird (*ibid.*, p. 664) showed that approximately the same toxic power was exhibited by all " equivalent " phenol solutions—*i.e.*, solutions of phenol in water containing different amounts of salt, but all in equilibrium with the same solution of phenol in some immiscible solvent (*e.g.*, kerosene).

A more precise investigation of the relation between the surface tensions and activities of such solutions being desirable, the system phenol–sodium chloride–water was chosen for this purpose. To determine the phenol activity in aqueous solutions containing salt, analysis of the vapour proved inadequate, the partial pressure of the phenol being too small to allow of accurate measurement, and a partition method in which amyl alcohol was used as the second solvent failed because the distribution of amyl alcohol itself was affected by the presence of salt. Paraffin oil, however, being nearly insoluble in water, was practically free from this disadvantage.

The concentration of phenol in paraffin in equilibrium with a saturated aqueous solution of the former is small (about 0·2 mole/litre). Unfortunately, from zero concentration up to fifth molar, the activity of phenol in paraffin is not directly proportional to the concentration (see Table I); otherwise, its determination would be very simple. Since phenol associates in water, the curve relating its activity in water to its concentration therein must be *concave* towards the concentration axis (*i.e.*, the activity increases more slowly than the concentration). The experimental curve relating the concentrations of phenol in paraffin in equilibrium to the corresponding concentrations in water was, however, *convex* towards the latter axis, showing, as might indeed have been anticipated, that phenol associates more rapidly in paraffin than in water.

An independent method of determining the phenol activity is therefore necessary in order that the concentrations of phenol in paraffin may be referred to the true activities of the former. From data supplied by Peddle and Turner (J., 1911, **99**, 691), it is possible to calculate the approximate activity of phenol in salt-free solution, up to 0·55*M*, if the effect due to heat of dilution be neglected. By referring these to the values in Table I, using a rough extrapolation to cover the higher phenol activities, we were able to draw a set of curves giving the relation between the concentration of phenol in the aqueous phase and the phenol activity. These curves were now initially concave towards the concentration axis.

Beyond a certain point, however, which corresponded to a 0·4*M*-

solution of phenol in pure water, the curves were inflected, becoming convex. This inflection was undoubtedly due to insufficient correction of the original data; at higher concentrations the effect of heat of dilution probably becomes of importance. Analysis of the freezing-point data by Lewis and Randall's method (constancy of j/m) also indicated that errors in the activity values might be expected to become considerable at concentrations much beyond the above. In particular, the graphical extrapolation necessary over the regions of higher activity is very sensitive to error.

It was decided, therefore, to assume that the activities, as calculated by the freezing-point method, were sensibly correct up to a value of about 0·3 (*i.e.*, that corresponding to a 0·4M-solution of phenol in pure water). Beyond this, the relation between activity and concentration was assumed to be expressed by a graphical extrapolation of each curve, preserving throughout the extrapolated region the curvature of its earlier portion. This procedure was in some measure justified (*a*) by the fact that for the curves relating to the higher salt concentrations the extrapolation was nearly linear, and (*b*) by the observation that if the corrected activities, as obtained separately from each of the curves, were all referred to a common diagram expressing the relation between phenol activity and concentration in paraffin solution, a set of points was obtained which lay, with very small deviations, on a single curve.

Finally, therefore, a smooth curve was drawn through these points, relating the concentration of phenol in paraffin to its corrected activity; and from this curve the values given in column IV of Table I were obtained. The results are shown in Fig. 1; curves I—VI give the activities of phenol in aqueous solutions containing 0, 5, 10, 15, 20, and 25 g. of sodium chloride per 100 c.c. of solution respectively. The nature of the second, graphical, correction of activities is shown in curve V, where the dotted curve indicates the inflection obtained at higher concentrations, using the extrapolation from the freezing-point data of Peddle and Turner.

The experimental procedure adopted to determine the partition of the phenol was as follows: 20 c.c. Portions of a phenol solution of known concentration were placed with 20 c.c. of paraffin oil in glass-stoppered bottles, to which weighed amounts of salt had been added, immersed in a thermostat at 20°. The mixtures were shaken vigorously and repeatedly for some hours, and 10 c.c. of the lower, aqueous, layer were then removed and the phenol content was estimated by Koppeschaar's method, using a standard solution of potassium bromate and bromide. The phenol content of the paraffin phase was estimated by difference, save in the case of those solutions which comprised *three-phase* mixtures: water + phenol +

salt, a phenol-rich phase, and phenol + paraffin. Of these mixtures, which are marked " saturated " in Table I, the aqueous phase was estimated as before; 10 c.c. of the paraffin phase were then removed, and shaken with an equal volume of water. From the amount of phenol passing into the water, it was possible, by means of previous measurements of the partition of phenol in the absence of salt, to estimate the amount of phenol present in the paraffin phase of the original mixture.

TABLE I.

Column I gives the concentration of sodium chloride in moles/litre; column I*a*, the salt concentration in g./100 c.c. of solution.

Salt conc.		Phenol concentration (mole/litre).		IV. Corrected
I.	I*a*.	II. In water.	III. In paraffin.	phenol activity.
0	0	0·069	0·014	0·067
		0·206	0·044	0·189
		0·419	0·098	0·345
		0·663	0·166	0·462
		0·889 (sat.)	0·228	0·526
0·855	5	0·064	0·019	0·090
		0·188	0·062	0·244
		0·304	0·111	0·374
		0·366	0·145	0·432
		0·510 (sat.)	0·265	0·550
1·71	10	0·059	0·024	0·110
		0·170	0·081	0·300
		0·214	0·111	0·374
		0·350 (sat.)	0·292	0·558
2·57	15	0·052	0·030	0·134
		0·147	0·103	0·356
		0·180	0·147	0·436
		0·236	0·281	0·556
3·42	20	0·046	0·036	0·158
		0·124	0·126	0·400
		0·146	0·179	0·476
		0·180	0·336	0·576
		0·182 (sat.)	0·353	0·580
4·28	25	0·040	0·043	0·180
		0·102	0·148	0·438
		0·114	0·211	0·508
		0·134	0·395	0·588

The Surface Tensions of Aqueous Phenol, and Phenol–Salt, Solutions.

In these experiments the phenol content was estimated by titration, and the surface tensions were determined by the drop-weight method, using the apparatus previously described (Goard and Rideal, this vol., p. 780). The densities of the solutions of sodium chloride were taken from Kohlrausch, the difference of density (which is small) due to the phenol being taken as directly proportional to the phenol concentration.

All measurements were made at 20°. The weight of ten drops

was ascertained, the mean weights given below being calculated from several closely concordant determinations.

Table II.

The first column gives the salt concentration in moles/litre, the second column the concentration in g./100 c.c. of solution.

Salt conc. I.	Salt conc. II.	Phenol conc. (mole/litre).	Mean wt. of 10 drops (g.).	Density.	Surface tension (dynes/cm.).
0	0	0·050	0·8442	0·999	67·88
		0·127	0·7473	0·999	60·10
		0·268	0·6398	1·000	51·58
		0·496	0·5550	1·003	44·97
		0·889	Surface tension taken from Part I		39·98
1·71	10	0·053	0·7988	1·064	64·26
3·42	20		0·7416	1·125	59·68
5·13	30		0·6749	1·182	54·61
6·15	36		0·6492	1·215	52·68
1·71	10	0·127	0·6811	1·065	55·14
3·42	20		0·6100	1·126	49·43
4·28	25		0·5616	1·154	45·32
4·70	27·5		0·5451	1·169	44·23
4·96	29		0·5452	1·180	44·18
1·71	10	0·223	0·5891	1·066	47·93
2·57	15		0·5489	1·097	44·48
2·98	17·5		0·5281	1·112	42·75
3·42	20		0·5243	1·127	42·50
0·85	5	0·344	0·5680	1·035	46·02
1·37	8		0·5449	1·053	44·15
2·05	12		0·5156	1·080	41·78
2·22	13		0·5121	1·086	41·59

In Fig. 2, the surface tensions of phenol solutions containing different amounts of salt (obtained by graphical means from Table II) are shown plotted against the logarithm of the corresponding phenol activities. Curves I—VI represent solutions containing 0, 5, 10 . . . 25 g. of salt per 100 c.c., respectively (corresponding thus to curves I—VI in Fig. I).

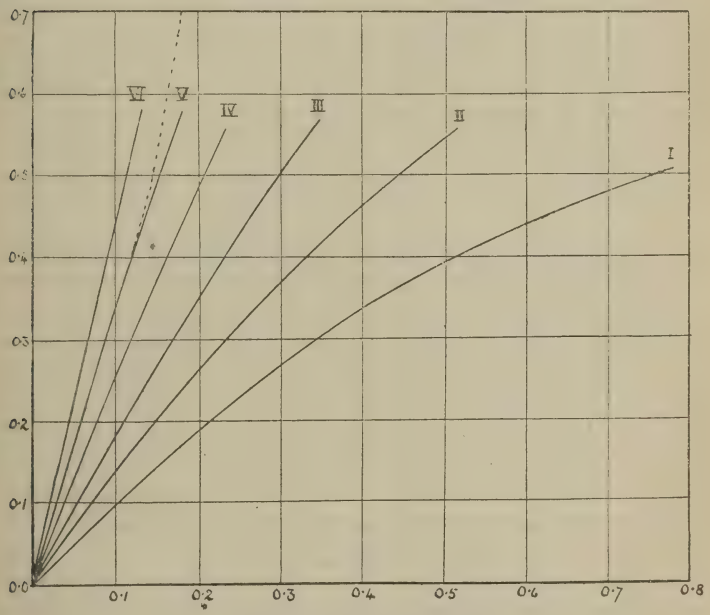
Considering first curve I, it will be observed that, as the activity of the phenol increases, the slope of the curve also increases, at first rapidly, then much more slowly, up to the point of saturation. The whole curve, in fact, strongly resembles those reproduced by Harkins for aqueous solutions of the lower fatty acids ("Surface Energy in Colloidal Systems," Chap. VI, Vol. I of "Colloidal Behaviour." Bogue, New York, 1924).

The maximum value of the adsorption, Γ, found by drawing a tangent to the curve at its steepest point, and taking the mean of several such determinations, is $69{\cdot}2 \pm 1 \times 10^{-11}$ g.-mol. per sq. cm. If we follow Langmuir (*J. Amer. Chem. Soc.*, 1917, **39**, 1848) in assuming that the surface layer is comprised in a unimolecular film, the area, A, occupied by a single molecule at the surface is

given by $A = 1/\Gamma N$, whence $A = 23{\cdot}8 \pm 0{\cdot}5 \times 10^{-16}$ sq. cm. The value found by Adam (*Proc. Roy. Soc.*, 1923, *A*, **103**, 676) in the cases of *p*-hexadecyl- and *p*-octadecyl-phenol was also 23·8 Å.U. This, he considers, represents the area of cross-section of the benzene nucleus. The agreement here can scarcely be accidental; it indicates that the molecules of ordinary phenol form a unimolecular film at the surface, the hydroxyl groups being drawn inwards, leaving the plane of the benzene nucleus at right angles to the surface.

FIG. 1.

Activity of phenol in aqueous solution.



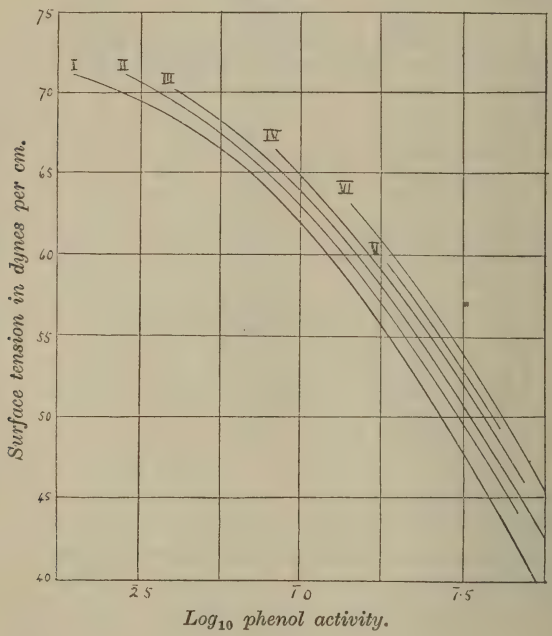
Mole of phenol per litre.

The thickness of the adsorbed layer can only be calculated by assuming a value for the density, which is probably nearly that of pure phenol. The density of solid phenol at 33° is 1·06; that of the phenol-rich phase formed at 20° is 1·05. The thickness of the adsorbed layer, taking the latter figure, is 6·4 Å.U. The probable length of the benzene ring is given by Adam as about 6 Å.U.

These values differ considerably from those given by Langmuir (*loc. cit.*), who, from data furnished by Morgan and Egloff (*J. Amer. Chem. Soc.*, 1916, **38**, 555, 844), deduces that the phenol molecule, of mean area 34 Å.U., lies flat on the surface of the solution. This difference is principally due to the fact that Langmuir assumed the

phenol activity to be throughout proportional to the concentration. If the present values for the surface tensions be plotted against the logarithms of the *concentrations*, the maximum apparent value of Γ is reached in the middle of the curve, at a concentration of phenol of about 0·2 mole/litre, after which there is a decrease of slope, and consequently a decrease in the apparent value of the adsorption, due to the fact that no allowance has been made for association of the phenol.

FIG. 2.



Considering now the curves formed by solutions of phenol containing salt, we see that they lie parallel to curve I, and have the same slope at corresponding activities. It follows that the amount of phenol adsorbed at the surface of equi-active phenol solutions is independent of the concentration of salt in the solution. The curves are, however, not coincident, showing that the salt has an effect on the actual value of the surface tension. The extent of the displacement of the curves shows this effect to be nearly the same as that of salt on pure water. At higher concentrations, however, the effect of salt on the phenol solutions diminishes, the curves for 15, 20, and 25% of salt being closer together than those for 0, 5, and 10%. With pure water, on the other hand, the effect increases as the salt solution becomes more concentrated.

Discussion of Results.

The results described in this paper do not seem to support the now well-known theory of surface tension proposed by Langmuir (*loc. cit.*) and Harkins (*op. cit.*), which maintains (1) that the surfaces of liquids containing asymmetric molecules consist of a unimolecular film of these molecules, oriented in such a way that their more active portions are drawn inwards, and (2) that " the surface energy of a liquid is thus not a property of the group molecules, but depends only on the least active portions of the molecules, and the manner in which these are able to arrange themselves in the surface layer " (Langmuir, *loc. cit.*). We have seen that there is good reason to suppose that the adsorbed layer at the surface of aqueous phenol solutions, at least when these approach saturation, consists of a unimolecular film of oriented phenol molecules. This is in accordance with the views of Langmuir; but further consideration must lead us to hesitate before ascribing, as this theory postulates, the actual surface tensions of the solutions entirely to the effect of the stray fields of force surrounding the outer layers of atoms.

Langmuir supposes the surface tension of an aqueous salt solution to consist of a unimolecular layer of oriented water molecules; but if these oriented molecules, by virtue of their stray fields, are alone responsible for the elevation of the surface tension, it is difficult to conceive that their effect should be largely unaltered by the presence at the surface of a closely packed layer of phenol molecules. Yet we have seen this to be the case. It would seem that, besides the effect of the surface film, it is necessary to take into account what may be called the " foundation " of the film. This is further indicated by the form of the curves obtained if the surface tensions given in Table II are plotted against salt concentration. The lowering of surface tension is at first nearly linear; with increasing salt concentration, the rate of fall increases somewhat up to a point of inflection, shortly after which a second phase separates; the surface tension varies very little beyond this point. Close inspection of the curves shows that there is no marked discontinuity at the " salting-out " point; for some little distance before the point is actually reached the rate of fall of surface tension diminishes, indicating possibly a thickening of the surface film of phenol molecules. Even here, however, the effect of the salt persists; since the actual value of the surface tension at different salting-out points varies with the salt concentration.

We must conclude, therefore, that although the presence of a unimolecular film of oriented phenol molecules at the surface is probably the chief factor in determining the surface tension,

the molecules at greater depths have also an influence upon it. Recent work by Iredale (*Phil. Mag.*, 1923, **45**, 1088; 1924, **48**, 177), Wilson (*Physical Rev.*, 1920, **16**, 8), and Terzaghi (*ibid.*, p. 54) indicates that molecular forces may be active over ranges considerably exceeding the length of a single molecule. A complete theory of surface tension should cover both the surface film and the "foundation" upon which that film rests.

DEPARTMENT OF PHYSICAL CHEMISTRY,
CAMBRIDGE UNIVERSITY. [*Received, May 10th*, 1925.]

CCXXII.—*Bromination of Acyl Derivatives of Phenylhydrazine. Preparation of 2 : 4-Dibromophenylhydrazine.*

By JAMES ERNEST HUMPHRIES and ROY EVANS.

BROMINATION, even with excess of the halogen, of the acetyl and benzoyl derivatives of phenylhydrazine in cold chloroform or carbon tetrachloride does not produce diazonium salts (compare Michaelis, *Ber.*, 1893, **26**, 2190; Vaubel, *J. pr. Chem.*, 1894, **49**, 540; 1897, **55**, 220). The formation of diazonium salt in Michaelis's experiment appears to have been due to the action of the bromine on phenylhydrazine formed from its acetyl derivative by hydrolysis by the hydrochloric acid used as solvent.

In our experiments, no evidence was obtained of the existence of *N*-bromo-compounds, proved by Chattaway (J., 1908, **93**, 852) to be formed in the bromination of phenylhydrazine.

The experiments were carried out at $-5°$ to $-10°$. After the initial experiments chloroform was used as solvent, since the acyl derivatives are more soluble in it than in carbon tetrachloride. The brominated phenylhydrazines produced were identified by conversion into the bromophenylhydrazones of benzophenone or benzaldehyde. Tests for diazonium compounds were carried out with an alkaline solution of β-naphthol.

Acetylphenylhydrazine. (1) Bromine (1 mol.) was added gradually to the solution, which became red and turbid. *Acetyl-p-bromophenylhydrazine hydrobromide* slowly separated as a white, crystalline solid, m. p. 132° (decomp.) (Found: total Br, 51·5; HBr, by titration with baryta, 26·4. $C_8H_9ON_2Br,HBr$ requires total Br, 51·6; HBr, 26·1%). The compound dissolved immediately in alcohol and from the solution acetyl-*p*-bromophenylhydrazine, m. p. 164°, was soon deposited (Found: Br, 34·7. Calc., Br, 34·9%).

(2) A solution of 12 g. (1 mol.) of acetylphenylhydrazine in 400 c.c. of chloroform was cooled to 0°, slowly treated with 8·2 c.c. (2 mols.) of bromine, and kept for 12 hours at the ordinary temperature, when the heavy, red oil that had separated solidified (from more dilute solutions it separated in crystals). The crystalline mass, which was washed with chloroform, was *acetyl*-2 : 4-*dibromophenylhydrazine hydrobromide*, m. p. 146° (decomp.); it decomposed in the air, giving off hydrogen bromide (Found: total Br, 61·85; HBr, 20·9. $C_8H_8ON_2Br_2$,HBr requires total Br, 61·7; HBr, 20·8%). The compound was dissolved in cold alcohol and water added to the solution, when acetyl-2 : 4-dibromophenylhydrazine, m. p. 146°, was formed in theoretical yield (24—25 g.) (Found: Br, 51·7. Calc., Br, 51·9%). The hydrochloride of the hydrazine was easily obtained by warming the acetyl derivative with concentrated hydrochloric acid.

Benzoylphenylhydrazine. The solution turned red and turbid when the bromine (2 mols.) was added and after a short time white needles of 2 : 4-dibromophenylhydrazine hydrobromide separated (Found: Br, 68·9. Calc., Br, 69·2%).

THE UNIVERSITY, ABERDEEN. [*Received, May 21st*, 1925.]

CCXXIII.—*The Structure of α-Campholytic Acid. A Correction.*

By JUAN PEDIGE CHARLES CHANDRASENA, CHRISTOPHER KELK INGOLD, and JOCELYN FIELD THORPE.

IN a previous paper (J., 1922, **121**, 1542) it was pointed out that the existing evidence of the structure of campholytic acid is equivocal: it could be used just as easily to support the bridged-ring constitution (I) as the accepted unsaturated structure (II). The possibility of a tautomeric form having structure (I) had not previously been considered, but it was suggested that the time had arrived to do so in view of the proved tautomerism between (III) and (IV) (compare Parts I and II of the same series).

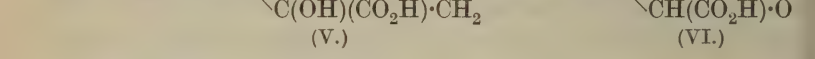


(I.) $CMe_2<\begin{matrix}CMe\text{——}CH_2\\ |\quad\quad |\\ C(CO_2H)\cdot CH_2\end{matrix}$ ⇌ $CMe_2<\begin{matrix}CMe\text{═══}CH\\ |\quad\quad |\\ CH(CO_2H)\cdot CH_2\end{matrix}$ (II.)

(III.) $CMe_2<\begin{matrix}C(CO_2H)\cdot CH_2\\ |\quad\quad |\\ CH\text{——}CO\end{matrix}$. ⇌ $CMe_2<\begin{matrix}C(CO_2H)\text{:}CH\\ |\quad\quad |\\ CH_2\text{——}CO\end{matrix}$ (IV.)

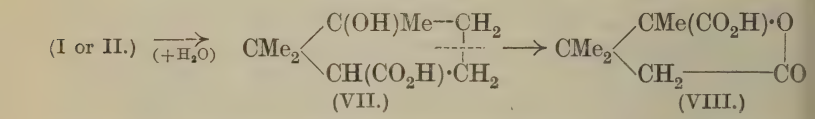
The object of the paper was, therefore, to advance unequivocal evidence favouring formula (I), and it was suggested that the oxid-

ation of campholytic acid to the lactonic acid (VI) might be regarded in that light:



(I.) (V.) (VI.)

The lactone (VI) has the same m. p. and almost the same properties as the isomeric lactone (VIII), which, of course, might arise from *either* (I) *or* (II), through (VII):



(I or II.) (VII.) (VIII.)

The lactone actually obtained, however, is not (VI), as was at first supposed, but (VIII); and so, again, the evidence of structure is ambiguous.

Structure (VI) was incorrectly assigned to the lactonic acid on the grounds of its identity with a specimen prepared from trimethylglutaric acid by Pandya and Thorpe (J., 1923, **123**, 2865), who, being misled by an erroneous statement of Balbiano (now corrected: this vol., p. 1072), wrongly regarded the substance as possessing formula (VI). The authors desire to express their regret that this mistake should have arisen.

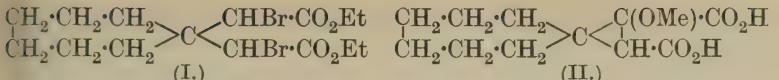
THE IMPERIAL COLLEGE, SOUTH KENSINGTON.
THE UNIVERSITY, LEEDS. [*Received, June 3rd,* 1925.]

CCXXIV.—*The Formation and Stability of* spiro-*Compounds. Part XII. Further Evidence for the Multiplanar Configuration of the* cyclo*Heptane Ring.*

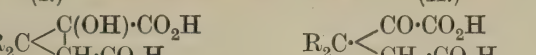
By JOHN WILLIAM BAKER.

BAKER and INGOLD showed (J., 1923, **123**, 122) that the original hypothesis of Beasley, Ingold, and Thorpe (J., 1915, **107**, 1080) fails, when applied to the *cyclo*heptane ring, in a manner suggesting that this ring, when once formed, is nearly strainless and therefore possesses multiplanar configuration.

To obtain confirmatory evidence, the action of hydrolysing agents on the dibromo-ester (I) and the methoxy-ring acid (II) has been investigated with the object of preparing either or both of the acids of types (III) or (IV).



(I.) (II.)



(III.) (IV.)

The relative stability of these acids (III) and (IV) forms an important criterion respecting the condition of strain in the *cyclo*heptane ring, for whilst in the dimethyl ($R_2 = Me_2$, angle 109·5°) and *cyclo*pentane series ($R_2 = C_4H_8>$, angle 108°) the open-chain keto-form is the stable modification, in the *cyclo*hexane series ($R_2 = C_5H_{10}>$, angle 120°) the strain in the three-membered *spiro*-ring is so far relieved that the hydroxy-ring acid becomes the stable isomeride; in intermediate cases, $R_2 = Et_2$ and Pr^{α}_2, a tautomeric equilibrium exists between the keto- and hydroxy-ring forms. If, therefore, the *cyclo*heptane ring is uniplanar as used to be supposed (angle 128·6°), its hydroxy*cyclo*propane compound of type (III) should be even more stable than the *cyclo*hexane analogue. If, on the other hand, the seven-membered ring is multiplanar, and therefore strainless or nearly so, it should resemble more closely its *cyclo*pentane analogue and the keto-acid (type IV) should be the stable modification.

The results obtained clearly indicate that the *cyclo*heptane ring is strainless, or nearly so,* for the open-chain keto-acid was the more stable isomeride, the hydroxy-ring acid (which was isolated) passing into the keto-acid under the conditions in which this reversible isomeric change has been observed in other cases.

On hydrolysis of the dibromo-ester (I) with boiling methyl-alcoholic potassium hydroxide the methoxy-ring acid (II), analogous in all respects to the corresponding *cyclo*hexane compound, was obtained. On hydrolysis with hydrobromic acid this methoxy-ring acid gave a large yield of a liquid acid and a very small yield of a solid acid which, although insufficient was obtained for analysis, was identified as *cyclo*heptane*spirocyclo*propane-1 : 2-dicarboxylic acid (V), the hydrobromic acid evidently having acted partly as a reducing agent.



(V.) (VI.)

The liquid acid, which was purified through its silver salt, proved to be the hydrated form (VI) of the keto-acid, for it readily

* Other investigators have reached the same conclusions on quite different grounds (compare Meerwein and his collaborators, *J. pr. Chem.*, 1922, **104**, 161, 289; Dickens, Horton, and Thorpe, J., 1924, **125**, 1830).

yielded a semicarbazido-acid on treatment with semicarbazide acetate.*

Hydrolysis of the dibromo-ester (I) with boiling 64% aqueous potassium hydroxide yielded (*a*) a small amount (about 1%) of the hydroxy-ring acid, (*b*) a large proportion of the above-mentioned hydrated keto-acid, and (*c*) a liquid lactonic by-product which, owing to an insufficiency of material, could not definitely be identified.

From these experiments, it appears that, in the presence of hot concentrated alkalis, a tautomeric equilibrium, greatly favouring the open-chain form, exists between the hydroxy-ring acid and the keto-acid.

Thus the *cyclo*heptane compounds resemble closely their *cyclo*pentane analogues, which contain a practically strain-free ring, and therefore it may be asserted with considerable confidence that the *cyclo*heptane ring also is nearly strainless as suggested in the earlier communication (*loc. cit.*).

It seems curious that the *cyclo*heptane ring should be multiplanar whilst the *cyclo*hexane ring shows no evidence of strainless configuration until joined to another ring in some such combination as is represented in decahydronaphthalene. This, however, can be accounted for if we assume with Mohr (*J. pr. Chem.*, 1918, **98**, 352) that these rings undergo vibrational interchange between the strainless and uniplanar phases, and further postulate that the uniplanar phase, which is more highly strained in the *cyclo*heptane than in the *cyclo*hexane series, is, for that reason, of much smaller duration in the former than in the latter type of ring.

Experimental.

The ethyl $\alpha\alpha'$-dibromo*cyclo*heptane-1 : 1-diacetate used was prepared as described by Baker and Ingold (*loc. cit.*). Since it cannot be distilled without passing into the bromolactone, the undistilled product was employed.

Hydrolysis of the Dibromo-ester (I).—(a) *With methyl-alcoholic potassium hydroxide.* cyclo*Heptane*spiro-1-*methoxy*cyclo*propane*-1 : 2-*dicarboxylic acid.* The dibromo-ester (5 g.) was added as rapidly as was consistent with safety to a boiling solution of potassium hydroxide (10 g.) in 30 c.c. of methyl alcohol, and boiling

* Incidentally an observation was made which probably explains the frequent failure to prepare semicarbazones of the ketoglutaric acids previously investigated. The *cyclo*heptane semicarbazido-acid is a stronger acid than acetic acid and under the ordinary conditions of semicarbazone formation takes sodium from the sodium acetate employed. Its mono- and di-sodium salts are sufficiently sparingly soluble to separate from the solution, but it may well be that in lower series such salts are too soluble to do likewise.

continued under reflux for a further 20 minutes. After evaporation of the alcohol, the residue was repeatedly extracted with ether, whence the methoxy-ring acid was obtained as a gum which slowly solidified. On crystallisation from ether–ligroin (b. p. 40—60°), it was obtained in large rosettes, m. p. 165° (Found: C, 58·7; H, 7·4; *M*, by titration, 121·3. $C_{12}H_{18}O_5$ requires C, 59·4; H, 7·5%; *M*, 121·1).

(b) *With* 64% *aqueous potassium hydroxide.* The dibromo-ester (5 g.) was added as rapidly as was consistent with safety to 45 c.c. of boiling 64% potash solution, and boiling continued for 20 minutes. The residue obtained from the ethereal extract of the cooled, diluted, and acidified product was a gum which was repeatedly extracted with warm water. The aqueous extract on evaporation left an almost colourless gum, from which a minute quantity of the hydroxy-ring acid (III) was slowly deposited as a white, crystalline solid (mixed m. p. determination).

The liquid fraction of the soluble portion, treated with semicarbazide hydrochloride in a saturated solution of sodium acetate, slowly deposited the white *disodium* salt of the semicarbazido-acid, which was drained on porous tile and crystallised from methyl alcohol–ethyl acetate, from which it separated as a crystalline powder, decomp. 240° (Found: Na, 14·3. $C_{12}H_{17}O_5N_3Na_2$ requires Na, 14·0%). Another portion of the gum was dissolved in dilute ammonia and the *silver* salt precipitated by the addition of silver nitrate to the neutral solution (Found: Ag, 46·8. $C_{11}H_{16}O_6Ag_2$ requires Ag, 46·9%).

The portion insoluble in water formed no semicarbazone derivative and from its general characteristics appeared to be the same hydroxy-lactone obtained when the bromo-lactone was hydrolysed with concentrated potash solution (Baker and Ingold, *loc. cit.*).

Hydrolysis of the Methoxy-ring Acid with Hydrobromic Acid.—*αα′-Dihydroxy*cyclo*heptane*-1 : 1-*diacetic acid* (VI). The methoxy-ring acid (0·75 g.) was heated under reflux with 7·5 c.c. of hydrobromic acid (*d* 1·49) for 2 hours, the hydrobromic acid evaporated off on the steam-bath, and the residue extracted with ether. The gum obtained from the ethereal extract deposited, after long standing, a small quantity of a crystalline acid, m. p. 215°, which depressed the m. p. of the hydroxy-ring acid but not that of the *cyclo*heptane *spiro*acid (V).

The portion which would not solidify, consisting of the hydrated form of the keto-acid, was dissolved in dilute ammonia, silver nitrate solution added to the neutral solution, and the precipitated *silver* salt (Found: Ag, 46·7. $C_{11}H_{16}O_6Ag_2$ requires Ag, 46·9%) washed successively with water, alcohol, and ether. The acid was

regenerated by warming the silver salt with hydrochloric acid and extracting with pure ether. On treatment with a solution of semicarbazide acetate, it deposited the white, crystalline *monosodium* salt of the semicarbazido-acid, which, treated like the disodium salt, was obtained as a white, crystalline powder, decomp. 235° [Found : C, 47·2 (corrected for the percentage of carbon which remained unburnt as sodium carbonate); H, 5·85; Na, 7·4. $C_{12}H_{18}O_5N_3Na$ requires C, 47·0; H, 5·9; Na, 7·5%].

A Correction.—The acid X (this vol., p. 987), described as a *bicyclo*heptane derivative, has since been found to be a lactonic acid derived from this by hydrolytic fission of the three-membered ring. The mechanism of the reaction is being further investigated.

The author desires to express his gratitude to Professor C. K. Ingold, F.R.S., for his kindly interest and advice during the progress of this investigation, and to the Research Fund Committee of the Chemical Society for a grant by which most of the expenses incurred in this research were met.

THE UNIVERSITY, LEEDS. [*Received, May 27th,* 1925.]

CCXXV.—*Tridentate Groups in Complexes of Tetrahedral and Octahedral Symmetry.*

By J. D. MAIN SMITH.

UNTIL 1912, the property of rotating the plane of propagation of polarised light had been invariably ascribed to the presence of " asymmetric atoms " in the molecules of compounds. In every case, each such characteristic atom was discernible as in direct association with four different atoms or atomic groups arranged tetrahedrally about the active atom. In 1911, Werner showed that optically active compounds could contain an " asymmetric atom " with which six atoms or atomic groups were octahedrally associated. His demonstration in 1912 of the existence of optically active compounds containing a cobalt atom octahedrally associated with three identical groups of atoms (chelate ethylenediamine molecules) led him to abandon the conception that optical activity is due to the presence of " asymmetric *atoms* " and to attribute optical activity to *molecular* asymmetry. Subsequent chemical evidence points strictly to the existence in optically active compounds generally, not of asymmetric atoms, but of asymmetric molecules, and, in the light of recent knowledge of the structure of atoms, it appears probable that every atom, at least so far as the outer structure is

concerned, possesses at least one plane of symmetry. Nevertheless, it is possible to discern in the molecule of every known optically *active* compound a central or nuclear atom about which the *asymmetry* of the molecule is focussed. This nuclear atom is the so-called asymmetric atom. In the case of optically *inactive* compounds, it is similarly possible to discern a central or nuclear atom about which the *symmetry* of the molecule is focussed. This atom, almost invariably that directly combined with the largest number of atoms or atomic groups, is the nuclear atom of Werner's co-ordination theory.

For the purposes of classification and nomenclature of chemical compounds it is necessary to select certain atoms in molecules as points of reference to which all other atoms in the molecule may be regarded as related. As the spatial relationships of atoms in molecules can be ascertained almost solely from considerations of symmetry, it is necessary to select the nuclear atom of a co-ordination complex as the point of reference, and to regard separately each atom directly attached thereto. An atom directly attached to a nuclear atom may itself be multivalent and may become the end member of an atomic group which may be considered as an entity or radical directly attached to the nuclear atom. Obviously such an atomic group may be attached directly to the nuclear atom by means of more than one atom, and atomic groups may thus be classified as unitary, chelate, and tridentate, respectively, according as they contain one, two, and three atoms directly attached to the nuclear atom.

The term "chelate group," used by Professor G. T. Morgan to indicate its claw-like attachment to a nuclear atom to form a cyclic system of linked atoms, may logically be extended to any atomic group which combines with a single atom to form a cyclic system, but it is convenient to restrict its use to those groups which yield heterocyclic systems when combined with nuclear atoms, usually metallic atoms.

Tridentate groups may be regarded as comprising three fused chelate groups and may be symbolised as ABC to indicate the three comprised chelate groups AB, AC, BC. Tridentate groups may be classified according to the number of different chelate groups comprised, and can be of only three types symbolised by AAA, AAB, and ABC, the first comprising three similar chelate groups, the second two similar chelate groups, and the third three different chelate groups.

Tridentate groups have long been known in organic chemistry, but invariably associated with so-called tetrahedral atoms. Removal of one of the median carbon atoms of naphthalene, for example,

leaves a typical tridentate group. Tridentate groups in inorganic chemistry were first identified by Werner in association with an octahedral nuclear atom, or more properly, with a nuclear atom having the co-ordination number six. The group $(NH_3)_3Co(OH)_3$, for example, was proved to be capable of uniting with another nuclear cobalt atom, both having the co-ordination number six, as in the complex ion

$$(NH_3)_3Co\overset{OH}{\underset{OH}{}}Co(NH_3)_3,$$

in which each $(NH_3)_3Co(OH)_3$ group is a tridentate group to the other Co atom. Prior to 1924, all the tridentate groups identified were found in complexes containing at least two octahedral nuclear atoms, as in the foregoing example. In that year, Pope and Mann (*Compt. rend.*, 1924, **178**, 2085) proved that $\alpha\beta\gamma$-triaminopropane was a group capable of triple attachment to a single metallic atom having the co-ordination number six, the cobaltic and rhodium compounds containing only two molecules of the tri-acidic base per metallic atom.

In view of the interest attaching to such compounds containing tridentate groups in uni-nuclear octahedral complexes, the results of the examination some years ago of the possibilities of tetrahedral and octahedral isomerism, due to association of tridentate groups with a single nuclear atom, are now published. A complete examination of the possibilities of tetrahedral and octahedral isomerism in complexes containing single atoms or unitary groups and also those containing chelate groups has already been published ("Chemistry and Atomic Structure," 1924, ch. VII). The following tables are based on the system of symbolisation there presented, with the necessary modifications for tridentate groups.

Only one main type of **tetrahedral** complex containing tridentate groups is possible, and consists of one tridentate group (symbolised by three capitals) and one unitary group (symbolised by lower-case letters). As shown above, only three variants of tridentate groups are possible, symbolised by AAA, AAB, and ABC, to indicate the various possible combinations of three fused chelate groups. This single type of tetrahedral complex is thus divisible into only three classes, (i) AAAb, (ii) AABc, and (iii) ABCd. The first class consists of a single optically inactive form, and the second and third each of two optically active (enantiomorphous) isomerides.

Three main types of **octahedral** complexes containing tridentate groups are possible, the first containing three single atoms or three unitary groups, the second containing one chelate group (indicated by two capitals) and one single atom or unitary group, and the third

containing two tridentate groups. Three single atoms or three unitary groups considered together can have only three variants, symbolised by aaa, aab, and abc. There can thus be no more than nine variants of one tridentate group with three unitary groups, and no more than nine variants of two tridentate groups. These two sets each of nine classes are shown in Table 1. As chelate groups can be of no more than two variants, symbolised by AA and AB, there can be no more than six variants of one tridentate group with one chelate group and one unitary group. These six classes are also shown in Table 1. The octahedral configuration containing tridentate groups can thus give rise to no more than three main types comprising 24 separate classes.

The various possible isomeric forms of any one class are differentiated into *cis*- and *trans*-forms according to whether the tridentate group is attached to three adjacent points forming a triangle on an imaginary octahedron about the nuclear atom or to three points two of which are octahedrally polar. In the *cis*-configuration the nuclear atom lies outside and in the *trans*-configuration within the plane containing the tridentate group.

With one exception, every optically inactive form containing a tridentate group contains at least one plane of symmetry. The exception is in the case of the inactive *cis*-form of the combination ABC ABC, which contains a centre of symmetry. This configuration is unique in that it is the sole inactive form of the 430 octahedral forms so far examined (75 with only unitary groups, 206 with chelate groups, and 149 with tridentate groups) which does not contain a plane of symmetry.

The following tables relate only to complexes which contain one nuclear atom, but the correct number of isomerides even for binuclear cases may be simply deduced by aid of the tables. If a tridentate group, or the chelate group, or a unitary group contain a nuclear atom so that the group as a whole is asymmetric, *i.e.*, not superposable on its mirror-image, every form shown in the tables as optically inactive will be optically active and an enantiomorphous form will be possible. The number representing the inactive forms is thus simply doubled and added to the number of active forms. Only one other special case need be considered. If in the combination ABC DEF, the tridentate groups are each asymmetric and in addition are mirror-images of one another, the number of possible optically active *cis*-forms will be reduced by two and one optically inactive form will take their place and will, like the inactive *cis*-combination ABC ABC, contain a centre of symmetry.

To illustrate the use of the tables in the determination of the number of possible isomeric forms of uni-nuclear complexes con-

taining tridentate groups, the compounds containing triaminopropane may be taken. This tridentate group comprises three chelate groups, of which two are similar, and the symbol for the group is thus AAB. The compounds prepared contained two tridentate groups per metallic atom, and thus belong to type 3,

TABLE I.

Types and Classes of Octahedral Symmetry.

	One tridentate group and		Two tridentate groups.
	No chelate group.	One chelate group.	
Class.	Type 1.	Type 2.	Type 3.
(i)	AAA bbb	AAA b CC	AAA AAA
(ii)	AAA bbc	AAA b CD	AAA BBB
(iii)	AAA bcd	AAB c DD	AAA BBC
(iv)	AAB ccc	AAB c DE	AAA BCD
(v)	AAB ccd	ABC d EE	AAB AAB
(vi)	AAB cde	ABC d EF	AAB CCD
(vii)	ABC ddd	—	AAB CDE
(viii)	ABC dde	—	ABC ABC
(ix)	ABC def	—	ABC DEF

TABLE II.

Isomeric Forms of Type 1 *with One Tridentate Group and No Chelate Group.*

Classes of type 1.	Optically active.			Optically inactive.			Grand Total.
	Cis.	Trans.	Total.	Cis.	Trans.	Total.	
(i) AAA bbb	—	—	—	1	1	2	2
(ii) AAA bbc	—	—	—	1	2	3	3
(iii) AAA bcd	2	—	2	—	3	3	5
(iv) AAB ccc	—	—	—	1	1	2	2
(v) AAB ccd	2	—	2	1	2	3	5
(vi) AAB cde	6	—	6	—	3	3	9
(vii) ABC ddd	2	—	2	—	1	1	3
(viii) ABC dde	6	2	8	—	1	1	9
(ix) ABC def	12	6	18	—	—	—	18
Totals	30	8	38	4	14	18	56

TABLE III.

Isomeric Forms of Type 2 *with One Tridentate Group and One Chelate Group.*

Classes of type 2.	Optically active.			Optically inactive.			Grand Total.
	Cis.	Trans.	Total.	Cis.	Trans.	Total.	
(i) AAA b CC	—	—	—	1	1	2	2
(ii) AAA b CD	2	—	2	—	2	2	4
(iii) AAB c DD	2	—	2	1	1	2	4
(iv) AAB c DE	6	—	6	—	2	2	8
(v) ABC d EE	6	2	8	—	—	—	8
(vi) ABC d EF	12	4	16	—	—	—	16
Totals	28	6	34	2	6	8	42

TABLE IV.

Isomeric Forms of Type 3 *with Two Tridentate Groups.*

Classes of type 3.	Optically active.			Optically inactive.			Grand Total.
	Cis.	Trans.	Total.	Cis.	Trans.	Total.	
(i) AAA AAA	—	—	—	1	1	2	2
(ii) AAA BBB	—	—	—	1	1	2	2
(iii) AAA BBC	—	—	—	1	1	2	2
(iv) AAA BCD	2	—	2	—	1	1	3
(v) AAB AAB	2	—	2	1	1	2	4
(vi) AAB CCD	2	—	2	1	1	2	4
(vii) AAB CDE	6	—	6	—	1	1	7
(viii) ABC ABC	10	2	12	1	—	1	13
(ix) ABC DEF	12	2	14	—	—	—	14
Totals	34	4	38	6	7	13	51

class (v), AAB AAB. Reference to Table IV shows that this class represents four isomeric forms, two optically active (enantiomorphous, *cis*-forms, one inactive *cis*-form, and one inactive *trans*-form. Pope and Mann's compounds may thus have been one or both of the inactive forms, the mixture (racemoid) of active forms, or a mixture of the racemoid forms with either or both of the inactive forms.

The results of the examination of the types, classes, and isomeric forms of tetrahedral and octahedral complexes containing a group contributing four to the co-ordination number of a nuclear atom will be communicated later, conclusive evidence having been obtained in these laboratories of the existence of a quadridentate group in both octahedral and tetrahedral complexes.

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CCXXVI.—*The Action of Halogens upon* m- *and* p-*Nitrobenzaldehydephenylhydrazones.*

By FREDERICK DANIEL CHATTAWAY and ARTHUR JOHN WALKER.

THE action of chlorine upon some arylhydrazones has been shown (Bülow, *Ber.*, 1918, **51**, 399) to result in the complete disruption of the hydrazone molecule and the formation of a diazonium chloride. This result might have been expected, since it had already been shown (Chattaway, J., 1908, **93**, 852; 1909, **95**, 958, 1065) that diazonium chlorides are produced quantitatively by the action of chlorine on arylhydrazines.

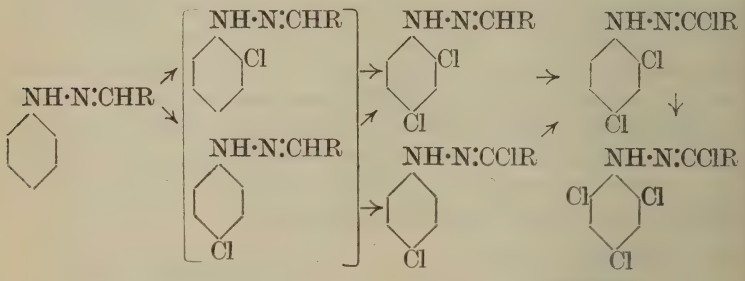
The stable nature of the nitrobenzaldehydephenylhydrazones renders it possible to follow more closely the action of chlorine upon them, since no appreciable breaking down of the molecule takes place during chlorination at the ordinary temperature.

When chlorine is passed in excess into a fine suspension in chloroform of *m*- or *p*-nitrobenzaldehydephenylhydrazone, the final product in each case is a tetra-substituted hydrazone, containing chlorine in the 2 : 4 : 6-positions of the hydrazine residue and also in the ω-position of the aldehyde residue :

$$C_6H_2Cl_3{\cdot}NH{\cdot}N{:}CCl{\cdot}C_6H_4{\cdot}NO_2.$$

If the chlorination be effected slowly, at various stages compounds can be isolated, the constitutions of which show that substitution in the two parts of the hydrazone molecule follows a similar course to that taken when acetanilide and benzaldehyde, respectively, are chlorinated.

Substitution in the ω-position of the aldehyde residue probably occurs to some extent from the first, but becomes more and more predominant as halogen enters the hydrazine nucleus. The main course of the substitution may be represented as follows, compounds not actually isolated being written in brackets (R = $C_6H_4{\cdot}NO_2$) :



As might be expected, the situation of the nitro-group in the aldehyde residue somewhat affects the course of the reaction, the chlorine entering the ω-position more easily when the nitro-group occupies the para-position.

As in the chlorination of the acetarylamides, the chlorine probably first replaces the hydrogen of the imino-group, and becomes transferred to the nucleus by a process of intramolecular rearrangement. These transformations must take place with great ease, for the product of the action of an excess of hypochlorous acid upon *m*-nitrobenzaldehydephenylhydrazone in the presence of potassium bicarbonate gives all the reactions of a nitrogen chloride and is very probably a mixture of ω-*chloro*-m-*nitrobenzaldehydechloroimino*-o- and -p-*chlorophenylhydrazones*, since on warming with hydrochloric acid it yields ω-*chloro*-m-*nitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone*.

All the ω-chloro-*m*- and -*p*-nitrobenzaldehydechlorophenylhydrazones, when heated with sodium acetate and acetic acid, are converted quantitatively into α-*acetyl*-β-*nitrobenzoylchlorophenyl*-

hydrazines identical with the compounds obtained by acetylating the corresponding nitrobenzoylchlorophenylhydrazines; *e.g.*,

$$C_6H_3Cl_2\cdot NH\cdot N{:}CCl\cdot C_6H_4\cdot NO_2 \xrightarrow{CH_3\cdot CO_2Na} C_6H_3Cl_2\cdot NAc\cdot NH\cdot CO\cdot C_6H_4\cdot NO_2.$$

The α-acetyl-β-nitrobenzoyl-*p*- and -2:4-dichlorophenylhydrazines, when heated with concentrated hydrochloric acid, are readily and completely hydrolysed into acetic acid, *m*- or *p*-nitrobenzoic acid, and the corresponding *p*- or 2 : 4-dichlorophenylhydrazine; *e.g.*,

$$C_6H_3Cl_2\cdot NAc\cdot NH\cdot CO\cdot C_6H_4\cdot NO_2 \xrightarrow{H_2O} CH_3\cdot CO_2H + C_6H_3Cl_2\cdot NH\cdot NH_2 + NO_2\cdot C_6H_4\cdot CO_2H.$$

Under similar conditions the corresponding α-acetyl-*m*- or -*p*-nitrobenzoyl-2 : 4 : 6-trichlorophenylhydrazine is not hydrolysed completely as might be expected, but yields *m*- or *p*-nitrobenzoic acid, and α-acetyl-2 : 4 : 6-trichlorophenylhydrazine, which is not easily broken down further; *e.g.*,

$$C_6H_2Cl_3\cdot NAc\cdot NH\cdot CO\cdot C_6H_4\cdot NO_2 \xrightarrow{H_2O} C_6H_2Cl_3\cdot NAc\cdot NH_2 + NO_2\cdot C_6H_4\cdot CO_2H.$$

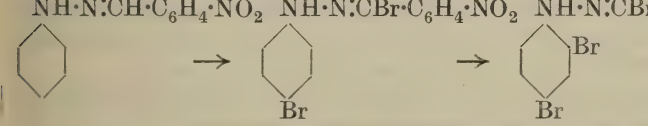
It seems probable that the firm attachment of the acetyl group in these compounds is to be attributed to the steric effect of the two *o*-substituted halogen atoms.

All ω-chloro-*m*- and -*p*-nitrobenzaldehydephenylhydrazones react with ammonia, forming *hydrazidines* by the replacement of the ω-chlorine atom by the amino-group; *e.g.*,

$$C_6H_2Cl_3\cdot NH\cdot N{:}CCl\cdot C_6H_4\cdot NO_2 \xrightarrow{NH_3} C_6H_2Cl_3\cdot NH\cdot N{:}C(NH_2)\cdot C_6H_4\cdot NO_2.$$

These are yellow or deep red basic compounds which all form colourless, well-crystallised hydrochlorides.

The action of bromine is similar to that of chlorine, although less energetic, direct substitution only leading to the introduction of two halogen atoms into the hydrazine residue, thus :



ω-*Bromo*-m- and -p-*nitrobenzaldehyde*-2 : 4 : 6-*tribromophenylhydrazones* are, however, easily obtained by the direct bromination of *m*- and *p*-nitrobenzaldehyde-2 : 4 : 6-tribromophenylhydrazones.

The behaviour of the ω-bromo-*m*- and -*p*-nitrobenzaldehyde-bromophenylhydrazones towards acetic acid and sodium acetate, and of the α-acetyl-β-nitrobenzoylbromophenylhydrazines towards hydrochloric acid, is exactly like that of the corresponding chloro-compounds.

The direct chlorination or bromination of any of the *m*- or *p*-nitrobenzaldehyde halogen-substituted phenylhydrazones naturally leads to the formation of an ω-substituted derivative; *e.g.*,

$$C_6H_4Cl\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot NO_2 \xrightarrow{Br} C_6H_4Cl\cdot NH\cdot N{:}CBr\cdot C_6H_4\cdot NO_2.$$

The ω-bromo-*m*- and -*p*-nitrobenzaldehydebromophenylhydrazones react with ammonia, forming *hydrazidines*, which are mostly deep red, basic compounds, which yield colourless salts.

Experimental.

Action of Chlorine upon m-*Nitrobenzaldehydephenylhydrazone.*

Unless effected cautiously, chlorination of *m*-nitrobenzaldehydephenylhydrazone resulted only in the separation of the final product, ω-*chloro*-m-*nitrobenzaldehyde*-2 : 4 : 6-*trichlorophenylhydrazone*. When carried out slowly, at intermediate stages m-*nitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone* and ω-*chloro*-m-*nitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone* separated from the solution. A smaller quantity of ω-chloro-*m*-nitrobenzaldehyde-*p*-chlorophenylhydrazone was also obtained.

ω-*Chloro*-m-*nitrobenzaldehyde*-2 : 4 : 6-*trichlorophenylhydrazone*, $C_6H_2Cl_3\cdot NH\cdot N{:}CCl\cdot C_6H_4\cdot NO_2$. Chlorine was passed to saturation into a cooled suspension of 5 g. of *m*-nitrobenzaldehydephenylhydrazone in 30 c.c. of chloroform, the dark solution which was first formed finally lightening in colour, and depositing the ω-*chloro*-m-*nitrobenzaldehyde*-2 : 4 : 6-*trichlorophenylhydrazone* as a grey, crystalline mass. This separated from acetic acid, in which it was only moderately soluble, in fine, colourless, hair-like needles, m. p. 157° (yield 5 g.) (Found: Cl, 37·6. $C_{13}H_7O_2N_3Cl_4$ requires Cl, 37·4%).

The same compound separated when chlorine was passed into a suspension of *m*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone in chloroform. A small quantity of the substance, when boiled with an alkaline solution of potassium permanganate, yielded *m*-nitrobenzoic acid, m. p. 140°, thus showing the absence of halogen in the aldehyde nucleus.

Isolation of m-*nitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone and* ω-*chloro*-m-*nitrobenzaldehyde*-p-*chlorophenylhydrazone*,

$C_6H_3Cl_2\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot NO_2$ and $C_6H_4Cl\cdot NH\cdot N{:}CCl\cdot C_6H_4\cdot NO_2$. Chlorine was cautiously passed into a suspension of *m*-nitrobenzaldehydephenylhydrazone (5 g.) in chloroform (30 c.c.) until the solution formed darkened and set to a solid brown mass, probably containing unstable compounds of the hydrazones with hydrogen chloride. On the addition of an equal volume of alcohol, it changed to a clean yellow, crystalline mass of *m*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone, m. p. 211° after recrystallisation from acetic

acid. The chloroform and alcohol mother-liquor slowly deposited crystals containing *ω-chloro*-m-*nitrobenzaldehyde*-p-*chlorophenylhydrazone*. After two recrystallisations from acetic acid this melted at 130°, but since further purification in this way was difficult, it was dissolved in boiling alcohol, a few c.c. of concentrated ammonia solution were added, the solution was acidified with concentrated hydrochloric acid, diluted with hot water, filtered, and made alkaline with ammonia; the *m*-nitrobenzaldehyde-*p*-chlorophenylhydrazidine which separated crystallised from alcohol in deep red needles, m. p. 150°, identical with the hydrazidine obtained from ω-bromo-*m*-nitrobenzaldehyde-*p*-chlorophenylhydrazone (p. 1694).

Isolation of ω-chloro-m-*nitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone*, $C_6H_3Cl_2\cdot NH\cdot N{:}CCl\cdot C_6H_4\cdot NO_2$. In another experiment, the passage of chlorine was cautiously continued until the brown precipitate containing *m*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone (above) just redissolved. The solution on standing, or on the addition of an equal volume of alcohol, yielded pale yellow crystals of *ω-chloro*-m-*nitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone*. This crystallised from acetic acid, in which it was moderately soluble, in long, pale yellow needles, m. p. 158° (yield 4 g.) (Found : Cl, 31·0. $C_{13}H_8O_2N_3Cl_3$ requires Cl, 30·9%).

The constitution of the compound was confirmed as follows : A mixture of 2 g. of β-*m*-nitrobenzoyl-2 : 4-dichlorophenylhydrazine and 3 g. (2 mols.) of phosphorus pentachloride was maintained for a few minutes at 190°, and the cooled product treated with water and extracted with ether. To the residue after evaporation were added a few c.c. of alcohol; the yellow solid which separated, m. p. 158° after recrystallisation from acetic acid, was identical with the chlorination product described above.

Action of Chlorine upon p-*Nitrobenzaldehydephenylhydrazone.*

ω-Chloro-p-*nitrobenzaldehyde*-2 : 4 : 6-*trichlorophenylhydrazone*. A cooled suspension of 5 g. of *p*-nitrobenzaldehydephenylhydrazone in 100 c.c. of chloroform was saturated with chlorine. The crystalline mass of *ω-chloro*-p-*nitrobenzaldehyde*-2 : 4 : 6-*trichlorophenylhydrazone* obtained separated from acetic acid, in which it was sparingly soluble, in fine, pale yellow needles, m. p. 164° (yield 6 g.) (Found : Cl, 37·5. $C_{13}H_7O_2N_3Cl_4$ requires Cl, 37·4%).

The same compound was obtained by the chlorination under similar conditions of *p*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone.

When boiled with an alkaline solution of potassium permanganate, it yielded *p*-nitrobenzoic acid, m. p. 238°.

Isolation of intermediate products in the chlorination of p-*nitro-*

benzaldehydephenylhydrazone. These products can be obtained with much greater ease than the analogous compounds formed in the chlorination of *m*-nitrobenzaldehydephenylhydrazone, the main products, *ω-chloro*-p-*nitrobenzaldehyde*-p-*chlorophenylhydrazone* and *ω-chloro*-p-*nitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone*, separating in good quantity at different stages of the reaction.

ω-Chloro-p-*nitrobenzaldehyde*-p-*chlorophenylhydrazone.* Chlorine was cautiously passed into a fine suspension in chloroform (5 g. in 100 c.c.) of *p*-nitrobenzaldehydephenylhydrazone, until the red solution first formed just became brown. Orange crystals of *ω-chloro*-p-*nitrobenzaldehyde*-p-*chlorophenylhydrazone* separated slowly, and a further quantity on addition of alcohol. It crystallised from acetic acid, in which it was moderately soluble, in orange needles m. p. 213° (yield 3 g.) (Found: Cl, 23·0. $C_{13}H_9O_2N_3Cl_2$ requires Cl, 22·9%). The same compound separated when *p*-nitrobenzaldehyde-*p*-chlorophenylhydrazone was similarly chlorinated. On boiling with alkaline permanganate solution, it yielded *p*-nitrobenzoic acid, m. p. 238°.

ω-Chloro-p-*nitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone.* The cautious passage of chlorine was continued beyond the stage described above, until the orange crystals of ω-chloro-*p*-nitrobenzaldehyde-*p*-chlorophenylhydrazone just redissolved. The solution almost immediately set to a mass of bright yellow crystals of *ω-chloro*-p-*nitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone.* This crystallised from acetic acid, in which it was sparingly soluble, in long, bright yellow, hair-like needles, m. p. 199° (yield 6 g.) (Found: Cl, 31·2. $C_{13}H_8O_2N_3Cl_3$ requires Cl, 30·9%).

The same compound separated when *p*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone was similarly chlorinated.

Conversion of ω-Chlorohydrazones into α-Acetyl-β-nitrobenzoylphenylhydrazines.—When the ω-chloro-*m*- and -*p*-nitrobenzaldehyde-chlorophenylhydrazones are boiled for 2 hours with an excess of anhydrous sodium acetate and acetic acid, they are quantitatively converted into the corresponding α-acetyl-β-nitrobenzoylchlorophenylhydrazines, which separate as solids when the acetic acid solutions are poured into water. They are best recrystallised from alcohol, in which the *p*-chloro-derivatives are easily soluble and the di- and tri-chloro-derivatives moderately easily soluble. These α-acetyl-β-nitrobenzoylchlorophenylhydrazines are readily hydrolysed when heated with a mixture of alcohol and hydrochloric acid, yielding ethyl acetate, the corresponding nitrobenzoic acid, and the hydrochloride of the corresponding hydrazine, a procedure which provides the easiest method of determining their constitution, and consequently that of the original ω-chlorohydrazones.

α-*Acetyl*-β-m-*nitrobenzoyl*-2 : 4-*dichlorophenylhydrazine*,

$$C_6H_3Cl_2\cdot NAc\cdot NH\cdot CO\cdot C_6H_4\cdot NO_2,$$

was obtained as described above from ω-chloro-*m*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone, and also directly from β-*m*-nitrobenzoyl-2 : 4-dichlorophenylhydrazine by boiling for a few minutes with acetyl chloride. It forms colourless plates, m. p. 155—156° (Found : Cl, 19·3. $C_{15}H_{11}O_4N_3Cl_2$ requires Cl, 19·3%).

The substance (1 g.) was boiled for 3 hours with 50 c.c. of alcohol and 20 c.c. of hydrochloric acid. The crystals of 2 : 4-dichlorophenylhydrazine hydrochloride that separated on cooling were identified by conversion into *o*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone, m. p. 192·5°. The mother-liquor was neutralised and alcohol and ethyl acetate were distilled off. On acidifying the residue and cooling, crystals of *m*-nitrobenzoic acid, m. p. 140°, separated.

α-*Acetyl*-β-p-*nitrobenzoyl*-p-*chlorophenylhydrazine*, obtained similarly, forms long prisms with domed ends, m. p. 167° (Found : Cl, 10·7. $C_{15}H_{12}O_4N_3Cl$ requires Cl, 10·6%). When boiled with alcohol and hydrochloric acid it yielded acetic acid, *p*-nitrobenzoic acid, and *p*-chlorophenylhydrazine.

α-*Acetyl*-β-p-*nitrobenzoyl*-2 : 4-*dichlorophenylhydrazine* crystallises in long, colourless, six-sided plates, m. p. 158° (Found : Cl, 19·4. $C_{15}H_{11}O_4N_3Cl_2$ requires Cl, 19·3%). When boiled with a mixture of hydrochloric acid and alcohol it yielded acetic acid, *p*-nitrobenzoic acid, and 2 : 4-dichlorophenylhydrazine.

α-*Acetyl*-β-m-*nitrobenzoyl*-2 : 4 : 6-*trichlorophenylhydrazine* was prepared as described above from ω-chloro-*m*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone, and also directly from β-*m*-nitrobenzoyl-2 : 4 : 6-trichlorophenylhydrazine by boiling for a few minutes with acetyl chloride. It crystallises in small, colourless prisms, m. p. 143° (Found : Cl, 26·3. $C_{15}H_{10}O_4N_3Cl_3$ requires Cl, 26·4%).

Hydrolysis of α-*Acetyl*-β-m-*nitrobenzoyl*-2 : 4 : 6-*trichlorophenylhydrazine to* m-*Nitrobenzoic Acid and* α-*Acetyl*-2 : 4 : 6-*trichlorophenylhydrazine*.—α-Acetyl-β-*m*-nitrobenzoyl-2 : 4 : 6-trichlorophenylhydrazine (4 g.) was boiled for 3 hours with 30 c.c. of alcohol and 20 c.c. of hydrochloric acid. On making alkaline with sodium carbonate and diluting with water, a colourless, oily liquid separated, which was removed. From the aqueous layer, on acidification, *m*-nitrobenzoic acid crystallised. The oily liquid did not crystallise alone or in contact with solvents. To its solution in warm alcohol *m*-nitrobenzaldehyde (2 parts) was added; on cooling, acetyl-*m*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone,

$$C_6H_2Cl_3\cdot NAc\cdot N{:}CH\cdot C_6H_4\cdot NO_2,$$

separated in colourless, rectangular plates, m. p. 204°, identical with

the substance obtained by the acetylation of *m*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone. The yield was 70%, and the original oily liquid from the hydrolysis must therefore have been mainly α-acetyl-2 : 4 : 6-trichlorophenylhydrazine, $C_6H_2Cl_3$·NAc·NH_2.

α-*Acetyl*-β-p-*nitrobenzoyl*-2 : 4 : 6-*trichlorophenylhydrazine* was prepared as above from ω-chloro-*p*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone, and also directly by boiling *p*-nitrobenzoyl-2 : 4 : 6-trichlorophenylhydrazine for a few minutes with acetyl chloride. It forms flat, colourless needles, m. p. 121° (decomp.) (Found : Cl, 26·4. $C_{15}H_{10}O_4N_3Cl_3$ requires Cl, 26·5%). When boiled with hydrochloric acid and alcohol, it behaves like the corresponding *m*-nitrobenzoyl derivative, yielding α-acetyl-2 : 4 : 6-trichlorophenylhydrazine as a colourless oil, and *p*-nitrobenzoic acid.

Conversion of ω-Chlorohydrazones into Hydrazidines.—In each case the ω-chloro-compound was boiled with alcohol and a slight excess of concentrated aqueous ammonia until the original solid had completely dissolved. The hydrazidine formed separated either during the reaction or on subsequent cooling. These hydrazidines are strongly coloured compounds which combine with hydrochloric acid (1 mol.) to form colourless salts that crystallise well when solutions of the bases in hot dilute hydrochloric acid are allowed to cool.

m-*Nitrobenzaldehyde*-p-*chlorophenylhydrazidine*,

$$C_6H_4Cl{\cdot}NH{\cdot}N{:}C(NH_2){\cdot}C_6H_4{\cdot}NO_2,$$

is very soluble in alcohol, from which it separates in deep red needles, m. p. 150° (Found : Cl, 12·3. $C_{13}H_{11}O_2N_4Cl$ requires Cl, 12·2%).

m-*Nitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazidine*,

$$C_6H_3Cl_2{\cdot}NH{\cdot}N{:}C(NH_2){\cdot}C_6H_4{\cdot}NO_2,$$

crystallises from alcohol, in which it is moderately easily soluble, in thin, irregular, orange plates, m. p. 154° (Found : Cl, 21·9. $C_{13}H_{10}O_2N_4Cl_2$ requires Cl, 21·75%). The *hydrochloride* is easily soluble in alcohol, less easily soluble in water. It separates from a mixture of these solvents in clusters of colourless needles, m. p. 220° (decomp.).

m-*Nitrobenzaldehyde*-2 : 4 : 6-*trichlorophenylhydrazidine* is sparingly soluble in alcohol, separating in fine, yellow leaflets, m. p. 194° (Found : Cl, 29·9. $C_{13}H_9O_2N_4Cl_3$ requires Cl, 29·6%). The *hydrochloride* forms colourless plates, m. p. 230° (decomp.), sparingly soluble in water and more soluble in alcohol.

p-*Nitrobenzaldehyde*-2 : 4 : 6-*trichlorophenylhydrazidine* crystallises from alcohol, in which it is moderately easily soluble, in dark red needles, m. p. 157° (Found : Cl, 29·8%). The *hydrochloride*, which is sparingly soluble in water, forms colourless, compact prisms, m. p. 260° (decomp.).

Action of Bromine upon m- *and* p-*Nitrobenzaldehydephenylhydrazones.*—The bromination of the nitrobenzaldehydephenylhydrazones was studied by Ciusa and Vecchiotti (*Gazzetta*, 1916, **46**, i, 240), who obtained the final products and, in the case of the *m*- and *p*-nitrobenzaldehydehydrazones, correctly regarded them as ω-bromonitrobenzaldehyde-2 : 4-dibromophenylhydrazones. They did not isolate the intermediate ω-bromonitrobenzaldehyde-*p*-bromophenylhydrazones.

ω-*Bromo*-m-*nitrobenzaldehyde*-p-*bromophenylhydrazone*,

$$C_6H_4Br{\cdot}NH{\cdot}N{:}CBr{\cdot}C_6H_4{\cdot}NO_2.$$

To a suspension of 5 g. (1 mol.) of *m*-nitrobenzaldehydephenylhydrazone in 100 c.c. of acetic acid was added a solution of 6 g. of bromine (slightly less than 2 mols.) in acetic acid. As the hydrazone dissolved, a yellow precipitate of the dibromo-compound separated, which crystallised from acetic acid, in which it was moderately easily soluble, in glistening, yellow plates, m. p. 146·5° (yield 6 g.). The use of less bromine caused the separation of the same compound in smaller amount, whilst the use of exactly 2 mols. of bromine led to the formation of small quantities of the tribromo-compound (Found : Br, 40·3. $C_{13}H_9O_2N_3Br_2$ requires Br, 40·1%). The same compound was also obtained by similarly brominating *m*-nitrobenzaldehyde-*p*-bromophenylhydrazone.

ω-*Bromo*-m-*nitrobenzaldehyde*-2 : 4-*dibromophenylhydrazone*. In a second experiment a larger quantity of bromine, 10 g. (3 mols.), was added, the ω-bromo-*m*-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone finally separating as a thick, crystalline mass. It crystallised from acetic acid in bright yellow needles, m. p. 179° (yield 7 g.) (Found : Br, 50·4%). The same compound was obtained by similarly brominating *m*-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone. When boiled with alkaline permanganate solution, it yielded *m*-nitrobenzoic acid, m. p. 140°.

The following ω-bromo-hydrazones were similarly prepared by the addition of bromine (1 mol.) to a suspension of the appropriate *m*-nitrobenzaldehydephenylhydrazone :

ω-*Bromo*-m-*nitrobenzaldehyde*-2 : 4 : 6-*tribromophenylhydrazone* crystallises in long, colourless, hair-like needles, m. p. 173°, sparingly soluble in acetic acid and alcohol (Found : Br, 57·7. $C_{13}H_7O_2N_3Br_4$ requires Br, 57·5%).

ω-*Bromo*-m-*nitrobenzaldehyde*-p-*chlorophenylhydrazone* crystallises from acetic acid, in which it is moderately easily soluble, in bright yellow, rectangular plates, m. p. 133° (Found : Cl + Br, 32·6. $C_{13}H_9O_2N_3ClBr$ requires Cl + Br, 32·6%).

ω-*Bromo*-p-*nitrobenzaldehyde*-p-*bromophenylhydrazone*,

$$C_6H_4Br{\cdot}NH{\cdot}N{:}CBr{\cdot}C_6H_4{\cdot}NO_2,$$

was prepared by the two methods described in the case of the isomeric *m*-nitro-derivative. It crystallises from acetic acid, in which it is moderately easily soluble, in light orange leaflets, m. p. 224° (Found: Br, 40·0%).

ω-*Bromo*-p-*nitrobenzaldehyde*-2 : 4-*dibromophenylhydrazone* separated when a solution of bromine (10 g.; 3 mols.) was added to a suspension in acetic acid of 5 g. of *p*-nitrobenzaldehydephenylhydrazone (1 mol.), or when bromine (1 mol.) was added to *p*-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone (1 mol.). It crystallises from acetic acid, in which it is sparingly soluble, in long, deep yellow needles, m. p. 214° (Found: Br, 50·2. $C_{13}H_8O_2N_3Br_3$ requires Br, 50·2%). When boiled with alkaline permanganate, the compound yielded *p*-nitrobenzoic acid, m. p. 238°.

By boiling the ω-bromohydrazones with sodium acetate in acetic acid α-acetyl-β-nitrobenzoylbromophenylhydrazines were obtained. These were recrystallised from alcohol, in which the monobromo-derivatives are more easily soluble than the dibromo-derivatives.

α-*Acetyl*-β-m-*nitrobenzoyl*-p-*bromophenylhydrazine*,

$$C_6H_4Br\cdot NAc\cdot NH\cdot CO\cdot C_6H_4\cdot NO_2,$$

was obtained from ω-bromo-*m*-nitrobenzaldehyde-*p*-bromophenylhydrazone as a colourless, amorphous solid which could not be made to crystallise. When boiled in alcohol with hydrochloric acid, it yielded acetic acid, *p*-bromophenylhydrazine, and *m*-nitrobenzoic acid.

α-*Acetyl*-β-m-*nitrobenzoyl*-2 : 4-*dibromophenylhydrazine* was obtained from ω-bromo-*m*-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone, and also from β-*m*-nitrobenzoyl-2 : 4-dibromophenylhydrazine, by boiling with acetyl chloride. It forms colourless, compact prisms, m. p. 169° (Found: Br, 35·1. $C_{15}H_{11}O_4N_3Br_2$ requires Br, 35·0%). When boiled with alcohol and hydrochloric acid, it yielded acetic acid, 2 : 4-dibromophenylhydrazine, and *m*-nitrobenzoic acid.

α-*Acetyl*-β-m-*nitrobenzoyl*-2 : 4 : 6-*tribromophenylhydrazine* crystallises from acetic acid, in which it is moderately easily soluble, in fine, colourless prisms, m. p. 180° (Found: Br, 44·7. $C_{15}H_{10}O_4N_3Br_3$ requires Br, 44·8%). On boiling for 3 hours with hydrochloric acid and alcohol, it yielded *m*-nitrobenzoic acid and a colourless, oily liquid. This formed a crystalline hydrazone (m. p. 230°) with *m*-nitrobenzaldehyde, identical with acetyl-*m*-nitrobenzaldehyde-2 : 4 : 6-tribromophenylhydrazone,

$$C_6H_2Br_3\cdot NAc\cdot N{:}CH\cdot C_6H_4\cdot NO_2,$$

obtained by the acetylation of *m*-nitrobenzaldehyde-2 : 4 : 6-tribromophenylhydrazone. The original oily liquid must therefore have been α-acetyl-2 : 4 : 6-tribromophenylhydrazine.

α-*Acetyl*-β-p-*nitrobenzoyl*-p-*bromophenylhydrazine* crystallises in colourless prisms, m. p. 169—170° (Found : Br, 21·25. $C_{15}H_{12}O_4N_3Br$ requires Br, 21·2%). When boiled with alcohol and hydrochloric acid, it yielded acetic acid, *p*-nitrobenzoic acid, and *p*-bromophenylhydrazine.

α-*Acetyl*-β-p-*nitrobenzoyl*-2 : 4-*dibromophenylhydrazine* forms stout, colourless octahedral crystals, m. p. 201—202° (Found : Br, 35·2. $C_{15}H_{11}O_4N_3Br_2$ requires Br, 35·0%). When boiled with hydrochloric acid and alcohol, it yielded acetic acid, *p*-nitrobenzoic acid, and 2 : 4-dibromophenylhydrazine. The same compound was prepared by boiling β-*p*-nitrobenzoyl-2 : 4-dibromophenylhydrazine with acetyl chloride for a few minutes.

The following hydrazidines were prepared from the corresponding ω-bromohydrazones by warming them with alcoholic ammonia.

m-*Nitrobenzaldehyde*-p-*bromophenylhydrazidine*,

$$C_6H_4Br\cdot NH\cdot N{:}C(NH_2)\cdot C_6H_4\cdot NO_2,$$

separates from alcohol, in which it is moderately easily soluble, in fine, dark red plates, m. p. 145° (decomp.). The *hydrochloride* crystallises in colourless plates, m. p. 200° (decomp.).

m-*Nitrobenzaldehyde*-2 : 4-*dibromophenylhydrazidine* separates from alcohol, in which it is very sparingly soluble, in small, dark red plates, m. p. 182° (decomp.) (Found : Br, 38·8. $C_{13}H_{10}O_2N_4Br_2$ requires Br, 38·6%). The *hydrochloride* forms colourless leaflets, m. p. 225° (decomp.).

p-*Nitrobenzaldehyde*-p-*bromophenylhydrazidine* crystallises from alcohol, in which it is moderately easily soluble, in almost black needles, m. p. 155° (decomp.) (Found : Br, 24·0. $C_{13}H_{11}O_2N_4Br$ requires Br, 23·9%). Its *hydrochloride* crystallises in colourless plates, m. p. 210° (decomp.).

p-*Nitrobenzaldehyde*-2 : 4-*dibromophenylhydrazidine* crystallises from alcohol, in which it is moderately easily soluble, in dark bronze-red needles, m. p. 175° (Found : Br, 38·7. $C_{13}H_{10}O_2N_4Br_2$ requires Br, 38·6%). The *hydrochloride* forms colourless, compact, rhombic plates, m. p. 200° (decomp.).

The following is a brief description of the hydrazones and hydrazines employed in confirming the structure of the α-acetylphenylhydrazines :

Acetyl-m-*nitrobenzaldehyde*-2 : 4 : 6-*trichlorophenylhydrazone*, prepared by boiling *m*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone for a short time with acetic anhydride, separates from alcohol, in which it is moderately easily soluble, in colourless, rectangular plates, m. p. 204° (Found : Cl, 27·4. $C_{15}H_{10}O_3N_3Cl_3$ requires Cl, 27·5%).

Acetyl-m-*nitrobenzaldehyde*-2 : 4 : 6-*tribromophenylhydrazone*, pre-

pared in a similar manner, crystallises from acetic acid, in which it is moderately easily soluble, in thick, colourless tablets, m. p. 230° (Found : Br, 46·0. $C_{15}H_{10}O_3N_3Br_3$ requires Br, 46·1%).

The following nitrobenzoylphenylhydrazines, prepared directly by the Schotten-Baumann method, were all crystallised from alcohol, in which they are moderately easily soluble.

β-m-*Nitrobenzoyl*-2 : 4 : 6-*trichlorophenylhydrazine ;* long, six-sided needles, m. p. 205° (Found : Cl, 29·6. $C_{13}H_8O_3N_3Cl_3$ requires Cl, 29·5%).

β-p-*Nitrobenzoyl*-2 : 4 : 6-*trichlorophenylhydrazine ;* stout, colourless plates, m. p. 203° (Found : Cl, 29·7. $C_{13}H_8O_3N_3Cl_3$ requires Cl, 29·5%).

β-m-*Nitrobenzoyl*-2 : 4-*dichlorophenylhydrazine ;* elongated, colourless plates, m. p. 196°.

β-m-*Nitrobenzoyl*-2 : 4-*dibromophenylhydrazine ;* colourless needles, m. p. 210° (Found : Br, 38·8. $C_{13}H_9O_3N_3Br_2$ requires Br, 38·5%).

β-p-*Nitrobenzoyl*-2 : 4-*dibromophenylhydrazine ;* pale yellow needles, m. p. 227°.

THE QUEEN'S COLLEGE, OXFORD. [*Received, March 18th,* 1925.]

CCXXVII.—*The Tautomerism of Dyads. Part IV. New Evidence of the Tautomeric Mobility of Oximes.*

By JOHN PREEDY GRIFFITHS and CHRISTOPHER KELK INGOLD.

THE purpose of this paper is to place dyad migration in oximes on a secure experimental basis such as has been provided in the cases of hydrogen cyanide, acetylene, and some monosubstitution products of the latter (E. H. Ingold, J., 1922, **121**, 1604; 1924, **125**, 1528; this vol., p. 1199), and to emphasise the suggestion, already made or foreshadowed by others (notably Brady and Dunn, J., 1916, **109**, 659; 1924, **125**, 291) that tautomerism of the dyad type, superimposed on the stereochemical theory of Hantzsch and Werner, constitutes the explanation of the isomerism and reactions of oximes.

$$[H]C{:}N \rightleftharpoons C{:}NH \qquad [H]C{:}\overset{|}{C} \rightleftharpoons C{:}\overset{|}{C}[H]$$

$$\text{(I.)}\quad [H]\overset{||}{N}{:}O \rightleftharpoons \overset{||}{N}{\cdot}O[H]\quad \text{(II.)} \qquad . \quad . \quad . \quad \text{(A)}$$

Whilst the retention of Hantzsch and Werner's stereochemical hypothesis is, for strong reasons, necessary to explain the isomerism of the oximes themselves, a structural addition to the theory is

just as imperatively required to account for their ethers (*Ann. Report*, 1924, p. 111).

(III.) $\begin{matrix} R\cdot C\cdot R' \\ \| \\ Alk\cdot N:O \end{matrix}$ (N-Ethers: *syn*- and *anti*-forms.)

$\begin{matrix} R\cdot C\cdot R' \\ \| \\ N\cdot OAlk. \end{matrix}$ (IV.) (O-Ethers: *syn*- and *anti*-forms.)

Formula (IV) for the O-ethers has long been generally approved, and, in view of evidence recently accumulated,* and of analogy with azoxy- and aliphatic diazo-compounds, no apology is necessary for using the "nitrone" formula (III), rather than the older *iso*oxime formula $\begin{matrix} RR'C—NAlk \\ \diagdown O \diagup \end{matrix}$, for the N-ethers.†

The study of tautomerism in numerous other cases has shown that the isolation of isomeric alkyl derivatives may be taken as an indication of the possibility of tautomeric interchange between parent hydrogen compounds of corresponding constitution. If, therefore, the structures given to the oxime-ethers (III) and (IV) be accepted, a *prima facie* case in favour of tautomerism of the dyad type between corresponding parent forms (I and II) is established (equation A).‡

Physical methods, which have the advantage of avoiding all the unknown disturbances attending the use of a chemical reagent, were applied to the problem; but, probably owing to the mobility of the oxime system, success was not achieved. Another method

* Thus towards diphenylketen, an almost universal reagent for double linkings, both the double bonds act separately (Staudinger and Miescher, *Helv. Chim. Acta*, 1919, **2**, 554):

$$>C:N:O \longrightarrow >C:N\begin{matrix}\diagup CPh_2 \\ \diagdown CO \\ \quad O\end{matrix} \longrightarrow CPh_2\begin{matrix}\diagup CO \\ \diagdown N \\ >C \quad O\end{matrix}\begin{matrix}\diagup CPh_2 \\ \diagdown CO.\end{matrix}$$

Many other examples might be given. Sugden's work (this vol., p. 1177) supplies strong confirmation from the physical side.

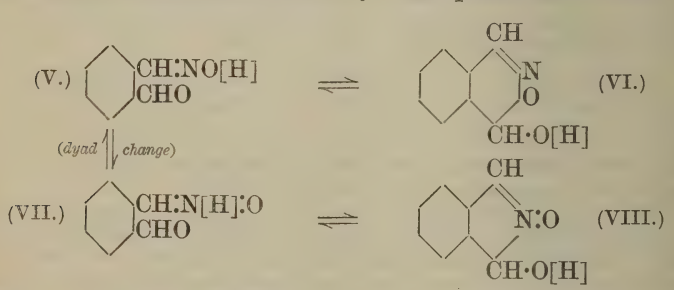
† If the nitrone structure be adopted, the existence of *syn*- and *anti*-N-ethers does not require an *ad hoc* extension of the Hantzsch-Werner hypothesis: it follows automatically from the optical resolution of amine-oxides, $R_1R_2R_3N:O$, just as the geometrical isomerism of ethylenes follows from the optical activity of methanes of the type $R_1R_2R_3R_4C$.

‡ It is not intended to preclude the intervention of the ring-form $\begin{matrix} >C—NR \\ \diagdown O \diagup \end{matrix}$ in certain decompositions, and, as an intermediate, in a few methods of formation of N-ethers and of oximes. Similarly, one cannot dismiss the nitroso-isomeride $>CH\cdot N:O$, which often constitutes an intermediate stage in reactions leading to oximes. All the available evidence shows, however, that these structures represent comparatively unstable oxime-forms, and may be looked upon as constituting minor ramifications of the tautomeric system, the main reversible reaction in which is, as will be shown, that represented by equation A.

of investigation was therefore sought, which, whilst still avoiding so far as possible, the complications arising from the use o reagents, would clearly and certainly distinguish between the tw expected forms and detect any equilibrium between them.

The object in view was ultimately attained by utilising th special properties of phthalaldehydemonoxime. This substance ordinarily represented by (V), contains all the essential feature which give ring-chain tautomeric character to a sugar, th residues –CH:O and –OH being present in such relative position that they can interact with the formation of an " oxide " rin and a " glucoside-yielding " hydroxyl group. If, therefore, th structure –CH:NOH, present in (V), be really one of the tauto meric forms of the oxime group, we should expect, just as in th case of a sugar, to be able to crystallise the cyclic tautomeric forn (VI). This individual, moreover, although a tautomeric substance should be sufficiently well differentiated chemically from any othe possible isomeride as to leave no doubt about its constitution, an therefore none about the particular oxime structure from whic it is derived.

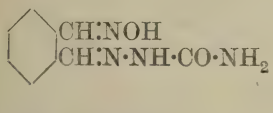
On the other hand, if an isomeride of the constitution (VII should also be present in any considerable quantity, the fact shoul be rendered evident by the tendency, possessed by this individua also, to pass into, and crystallise in the form of, its ring tautomeride (VIII). This structure, based on the *iso*indole ring system, als is strikingly differentiated from any other possible isomeride :



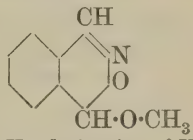
Thus the chemical differences to be expected from the simple dyad change (V) $\rightleftharpoons$ (VII) become magnified by the production, through ring closure, of the more distinctive structures (VI) and (VIII). At the same time, the mobile dyad equilibrium becomes partly " set " through association with the slower ring-chain changes. These are just the conditions which are required to render the dyad change open to experimental confirmation.

All these theoretical anticipations have been realised experimentally.

The ring form (VI), which was isolated in the crystalline condition, exhibited clear evidence of its constitution and of its structural analogy with the reducing sugars; it showed the usual aldehydic reactions (of the open-chain form V), yielding, for instance, the *semicarbazone* (IX), and also united readily with methyl alcohol, giving a *methyl* derivative *devoid of aldehydic properties*. This must therefore be derived from (VI) by the replacement of the bracketed hydrogen atom, and all its reactions, for instance, the ease with which it is hydrolysed back to the parent substance by a small quantity of mineral acid, emphasise its resemblance to a glucoside and leave no doubt as to the correctness of formula (X).



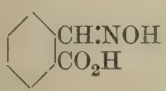
(IX; derivative of V.)



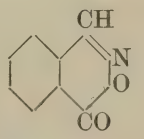
(X; derivative of VI.)

It is clear, therefore, that in solutions of the substance under discussion we have the ring-chain tautomeric system (V) $\rightleftharpoons$ (VI).

A closer study proved, moreover, that the principal phase in solution, as well as the solid substance itself, is represented by the ring-formula (VI). Thus, in contrast to the completeness and rapidity with which the "glucosidic" methyl derivative (X) is formed from freshly-prepared solutions of the parent, the aldehydic reactions of the latter, *e.g.*, the formation of the semicarbazone (IX), are noticeably sluggish: a solution of (VI), treated after some time with semicarbazide acetate, deposits a small quantity of the semicarbazone, but the complete precipitation of this substance requires a considerable period; and if a freshly-prepared solution of (VI) is used, no initial deposition is observed. It is noteworthy also that, although the main product of the oxidation of (VI) by cold neutral permanganate is *o*-carboxybenzaldoxime anhydride (XII), evidently derived directly from the ring compound, a small amount of the oxime-acid (XI), the normal product of oxidation of (V), is formed simultaneously. Observations of this kind make it quite evident that, as with sugars, the ring phase is the more stable one.



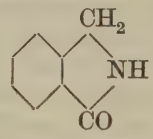
(XI; by-product.)

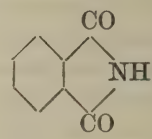


(XII; main product.)

Evidence of the existence of a second oxime structure (VII) was obtained by the isolation of a second ring-compound (VIII), which

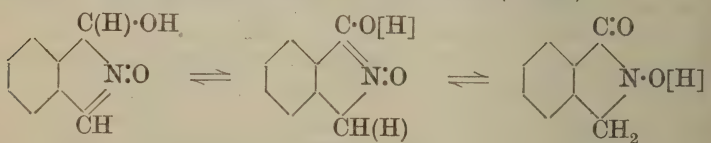
resembled the first in certain respects (for instance, in the absence from its methylation product of all aldehydic properties), but differed markedly from it in others. The key to its constitution was found in the fact that on reduction it gave phthalimidine (XIII), thus revealing the presence of the heterocyclic nucleus on which the anticipated formula (VIII) is based.

(XIII.) 

 (XIV.)

On oxidation phthalimide (XIV) was obtained.

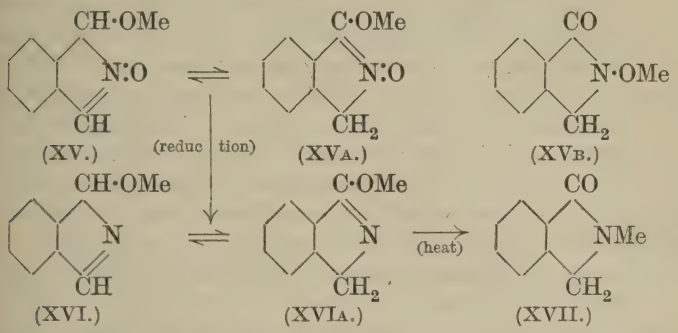
Closer examination showed, however, that the substance is not adequately represented by formula (VIII) alone, but that it is capable of reacting in several forms. This is to be expected. Obviously a substance of formula (VIII) would be susceptible to the type of triad change which is apparently common to all compounds containing an unsaturated five-membered ring fused to the benzene nucleus, as in indene, benzimineazole, and aziminobenzene (Ingold and Piggott, J., 1922, **121**, 2381). The second individual involved in this kind of tautomeric interchange would have formula (VIIIA). This, however, contains a system of the type known to undergo the "tetrad" change into an *N*-hydroxy-isomeride (Bamberger, *Annalen*, 1920, **420**, 137), and it should therefore pass reversibly into an individual of the formula (VIIIB).



(VIII.) (VIIIA.) (VIIIB.)

There is experimental evidence favouring all these formulæ. First, whilst any of the three forms might yield phthalimidine on reduction, only (VIII) can adequately account for aldehydic reactions depending on the opening of the heterocyclic ring. In addition, however, the compound forms a yellow sodium salt and an intensely coloured iron salt; and (VIII) cannot account for this, although either of (VIIIA) and (VIIIB) can do so. Finally, the compound forms two isomeric *methyl* derivatives. One of these, the main product, is obviously an *N*-methoxy-compound, derived from (VIIIB), for, unlike its isomeride, it cannot be reduced to a phthalimidine without previous hydrolysis; this methyl derivative is therefore represented by formula (XVB). The second methyl derivative (by-product) is a *C*-methoxy-compound, derived from

either (VIII) or (VIIIA), as is proved by the fact that it yields *O-methylphthalimidine* (XVI or XVIA) on reduction; the by-product must therefore be represented either by (XV) or by (XVA), or, more probably, by both.



O-Methylphthalimidine readily passes into *N*-methylphthalimidine (XVII), a type of isomeric change which is not uncommon and has for long been exemplified by the transformation of cyanuric into *iso*cyanuric esters on heating.

Further details with regard to the cyclic and aldehydic reactions of the compounds (VI) and (VIII), and the conditions of their interconversion, will be found in the experimental portion of this paper; but the summary already given will be sufficient indication as to the manner in which the isolation and study of these compounds establishes the fundamental dyad change of the oxime group.

EXPERIMENTAL.

Phthalaldehyde was prepared by hydrolysing with aqueous alcoholic potassium oxalate the ωωω′ω′-tetrabromoxylene obtained by brominating boiling *o*-xylene (Thiele and Gunther, *Annalen*, 1906, **347**, 107).

1-*Hydroxy*-2 : 3-*benzoxazine* (VI).—Phthalaldehyde (13·4 g.), dissolved in 30 c.c. of methyl alcohol, was gradually mixed in the cold with an aqueous solution (200 c.c.) of hydroxylamine prepared from 6·9 g. of hydroxylamine hydrochloride and 5·4 g. of anhydrous sodium carbonate. After a few minutes, the solution was extracted with much ether, and the extract washed with water, dried with calcium chloride by shaking, concentrated, and seeded with a crystal of hydroxybenzoxazine obtained from a previous experiment, when the substance crystallised (70% yield). A further quantity could be obtained from the ethereal mother-liquor, which also contained, however, some of the isomeric hydroxy*iso*indole oxide. Extraction of the aqueous mother-liquor with ethyl acetate yielded

a further quantity of the latter substance. If, however, at an stage of these extractions the aqueous solution was set aside fo a time, the unextracted material became converted into the methoxy benzoxazine described below.

On one or two occasions the preparation of hydroxybenzoxazin by the process described above failed for reasons that we have no been able to discover, almost the sole product being hydroxy*iso* indole oxide. Other cases of failure, resulting in the productio of the methoxy-compound, were traced to undue delay in pro ceeding with the extraction or removing the methyl alcohol fron the ethereal extract. On the other hand, during the preliminary experiments the desired hydroxybenzoxazine could sometimes b produced under quite a variety of conditions (see p. 1705).

1-*Hydroxy*-2 : 3-*benzoxazine* separates from ether–ligroin in prisms m. p. 114—115° (Found: C, 64·5; H, 4·7; N, 9·5. $C_8H_7O_2N$ requires C, 64·4; H, 4·7; N, 9·4%). It is very soluble in ethy acetate, easily soluble in chloroform or ether, but almost insoluble in ligroin. It reduces Fehling's solution. Its action towards methy and ethyl alcohols, oxidising agents, and other ketone reagents is described below. Attempts were made to reduce it both in acid and in alkaline solution under various conditions, including those described on pp. 1706–7, but without success, deeply coloured amorphous products being obtained which could not be purified No phthalimidine was obtained.

1-*Methoxy*-2 : 3-*benzoxazine* (X).—This may be obtained (*a*) by leaving phthalaldehyde in contact with hydroxylamine (1 mol.) in 30% methyl alcohol, when the compound crystallises; (*b*) from hydroxybenzoxazine by boiling with methyl alcohol, preferably in the presence of a trace of hydrochloric acid; (*c*) from hydroxy-*iso*indole oxide by digesting for several days with faintly acidified aqueous methyl alcohol, and then diluting. It separates from ether in glistening plates, m. p. 77° (Found: C, 66·3; H, 5·6; N, 8·7. $C_9H_9O_2N$ requires C, 66·3; H, 5·5; N, 8·6%). It is hydrolysed with great ease with dilute hydrochloric acid, giving hydroxy-benzoxazine.

1-*Ethoxy*-2 : 3-*benzoxazine* was prepared like the methoxy-compound, ethyl alcohol being used in place of methyl alcohol. It was obtained crystalline, but, as it tended to separate as an oil from all solvents in which it was not extremely soluble, it was not purified for analysis.

Phthalaldehyde-1-*oxime*-2-*semicarbazone* (IX).—The formation of this substance from hydroxybenzoxazine was studied in some detail and the main results have already been described (p. 1701). The semicarbazone itself can be purified in small quantities by rapid

crystallisation from ethyl acetate, from which a microcrystalline powder separates, m. p. 235° (decomp.) (Found: C, 52·7; H, 5·0. $C_9H_{10}O_2N_4$ requires C, 52·4; H, 4·9%).

Phthalaldehyde-1-*oxime*-2-p-*nitrophenylhydrazone*, prepared from hydroxybenzoxazine like the corresponding semicarbazone, and also from hydroxy*iso*indole oxide by digesting with *p*-nitrophenylhydrazine in acetic acid solution, separated from ethyl acetate in small, yellow prisms, m. p. 175° (decomp.) (Found: C, 59·0; H, 4·4. $C_{14}H_{12}O_3N_4$ requires C, 59·2; H, 4·2%).

Oxidation of 1-*Hydroxy*-2 : 3-*benzoxazine: Formation of* o-*Carboxybenzaldoxime and its Anhydride* (XI and XII).—The hydroxybenzoxazine, dissolved in pure ether, was shaken with successive small quantities of 1% potassium permanganate solution (in all, equiv. to 1 atom of oxygen) containing an excess of magnesium sulphate, the mixture was filtered, extracted with ether, and the aqueous solution acidified and again extracted. *o*-Carboxybenzaldoxime anhydride was recovered from the first extract and was identified by its m. p. (186°) and by its conversion into phthalimide on heating. The small amount of *o*-carboxybenzaldoxime obtained from the second extract was identified by its m. p. (120°) and by converting it into the anhydride.

1(*or* 3)-*Hydroxy*iso*indole*-2-*oxide* (N-*Hydroxyphthalimidine*) (VIII, etc.).—It is difficult to give precise directions for the preparation of this substance, for not only was it frequently obtained as almost the sole product on repeating as exactly as possible an experiment which had previously yielded hydroxybenzoxazine, but, on other occasions, attempts to repeat a successful preparation of hydroxy*iso*indole oxide gave hydroxybenzoxazine instead. It is believed that accidental seeding is, at any rate partly, responsible for these erratic results. Two circumstances, however, appear definitely to increase the chances of producing hydroxy*iso*indole oxide, namely, (*a*) the presence of alkalis, (*b*) a high temperature. Condition (*a*) can readily be understood, since hydroxy*iso*indole oxide yields a rather stable sodium salt, the formation of which would disturb any equilibrium involving hydroxy*iso*indole oxide, in such a way as to favour the ultimate isolation of this substance at the expense of hydroxybenzoxazine. Condition (*b*) is explicable if, in the dyad equilibrium between (V) and (VII) (p. 1700), a rise of temperature favours the (usually) less permanent form (namely, VII) just as in the cases of hydrogen cyanide and acetylene. The following typical experiments illustrate the employment of these two methods.

(i) The procedure leading to the formation of hydroxybenzoxazine (p. 1703) was repeated, excepting that 6·5 g. of anhydrous sodium

carbonate were employed instead of 5·4 g., the solution being neutralised before the extraction, which was carried out with chloroform in place of ether.

(ii) The procedure detailed on p. 1703 was followed with the exception that all solutions were previously heated at 60°, and mixed at this temperature. The extraction was carried out with ethyl acetate instead of ether, the extract being washed with water and roughly dried by sodium sulphate before evaporation.

The same substance can also be prepared by allowing hydroxybenzoxazine to remain dissolved in solvents (other than alcohols or ketones), or by digesting it with dilute aqueous sodium carbonate and acidifying. 1-Hydroxy*iso*indole-2-oxide separates from chloroform in well-defined prisms, m. p. 181° (Found : C, 64·3; H, 4·8; N, 9·4. $C_8H_7O_2N$ requires C, 64·4; H, 4·7; N, 9·4%). It is readily soluble in chloroform or ethyl acetate, sparingly soluble in ether, and nearly insoluble in water or ligroin. It is soluble in dilute mineral acids, giving colourless solutions, and it is also dissolved by aqueous sodium carbonate (or sodium hydroxide), giving a yellow solution containing a sodium salt, which is precipitated as a yellow powder when an ethyl acetate solution of the hydroxy-compound is mixed with ethereal-alcoholic sodium ethoxide. Ferric chloride gives an intense violet colour, the reaction constituting a delicate test for the substance in dilute solution. It also readily reduces Fehling's solution on warming, and, on digesting with an acetic acid solution of *p*-nitrophenylhydrazine acetate, gives the hydrazone above mentioned. Its action towards oxidising and reducing agents and its behaviour on methylation are described below.

Reduction of 1-*Hydroxy*iso*indole-2-oxide to Phthalimidine* (XIII).—(i) The substance (1 g.), dissolved in 3 c.c. of methyl alcohol, was treated gradually at 50—60° with 32 g. of 3% sodium amalgam, the solution being kept only faintly alkaline by successive additions of glacial acetic acid. After removal of the mercurial layer, the liquid was evaporated to dryness in a vacuum, and the solid residue extracted with warm ethyl acetate, from which crystals of nearly pure phthalimidine separated (m. p. 145—149°). On crystallisation from benzene, it had the correct m. p. (150—151°), and it was then definitely identified by analysis (Found : C, 71·9; H, 5·5. Calc., C, 72·2; H, 5·5%), and by conversion into its nitroso-derivative (m. p. 156°).

(ii) The hydroxy*iso*indole oxide was dissolved in dilute acetic acid and treated with an excess of zinc dust, added sufficiently rapidly to bring the solution to its boiling point towards the end of the process. An excess of ammonia was then added and the

solution extracted with ether, when an almost quantitative yield of phthalimidine was obtained.

(iii) Hydroxy*iso*indole oxide was dissolved in dilute acetic acid and treated with sodium amalgam in the cold, glacial acetic acid being added as required to keep the solution acid. The mercury was separated, an excess of sodium hydroxide added, and the phthalimidine extracted with ether (yield nearly quantitative).

Oxidation of 1-*Hydroxy*iso*indole*-2-*oxide to Benzaldoxime*-o-*carboxylic Acid* (XI) *and Phthalimide.*—This oxidation was carried out like that described on p. 1705 excepting that ethyl alcohol was used in place of ether and that no magnesium sulphate was added. No product was obtained on extracting the filtered solution with ether, but on acidifying and again extracting, a mixture of phthalimide and benzaldoxime-*o*-carboxylic acid was obtained, from which the former was readily separated owing to its smaller solubility in water.

N-*Methoxyphthalimidine* (IXB).—The hydroxy*iso*indole oxide was dissolved in methyl alcohol and treated with the theoretical quantity of methyl-alcoholic sodium methoxide, and then with twice the theoretical amount of methyl iodide. After heating on the water-bath for ½ hour, the excess of methyl iodide and the methyl alcohol were evaporated and the residue was mixed with water and extracted with ether, from which, on evaporation, long needles were obtained, m. p. 74° after crystallisation from ether–ligroin (a mixture with the isomeric methoxy-compound of m. p. 77° melted at 45°) (Found: C, 66·1; H, 5·6. $C_9H_9O_2N$ requires C, 66·3; H, 5·5%). The substance is readily soluble in benzene, ethyl acetate, chloroform, or ether, moderately soluble in ligroin, and insoluble in water. It does not dissolve in alkalis, gives no colour with ferric chloride, does not reduce Fehling's solution, and gives no condensation products with semicarbazide or the arylhydrazines.

Reduction of N-*Methoxyphthalimidine to Phthalimidine.*—Attempts to reduce this substance in neutral solution with zinc dust, ammonium chloride and aqueous methyl alcohol, or in water or dilute acetic acid with sodium amalgam, resulted in the recovery of unchanged material. Reduction took place, however, with tin and hydrochloric acid, and, on pouring the solution into an excess of alkali and extracting with ether, phthalimidine was obtained.

Oxidation of N-*Methoxyphthalimidine to Hydroxy*iso*indole Oxide and Phthalimide.*—The oxidation was carried out in neutral solution by permanganate in presence of magnesium sulphate as described on p. 1705, excepting that sufficient permanganate solution was used to supply three atoms of oxygen. On extraction with ether, a mixture of hydroxy*iso*indole oxide and phthalimide was obtained,

which were separated from each other by fractional crystallisation from ethyl acetate and identified by direct comparison with authentic specimens.

1(*or* 3)-*Methoxy*isoindole-2-*oxide* (IX or IXa) was obtained from the ultimate ether and ether–ligroin residues obtained in the methylation experiment described on p. 1707. The residues from several such experiments were evaporated and then extracted repeatedly with hot ligroin (b. p. 60—70°). On cooling in a freezing mixture, small prisms separated, m. p. 52—53° after softening at 48°, and from the oily residue obtained by evaporation of the ligroin a further quantity of the same substance was isolated by seeding (Found : C, 66·0; H, 5·7. $C_9H_9O_2N$ requires C, 66·3; H, 5·5%). It is readily soluble in all organic solvents, even ligroin, but insoluble in water. It is also insoluble in sodium carbonate solution, but readily soluble in dilute acids. It does not give a colour with ferric chloride, does not reduce Fehling's solution, and gives no condensation products with semicarbazide or the aryl-hydrazines.

*Reduction of Methoxy*isoindole-2-*oxide to* o-*Methylphthalimidine* (XV or XVa).—The substance was treated with successive quantities of zinc dust in a boiling aqueous methyl-alcoholic solution of ammonium chloride, and the filtered solution was evaporated to remove methyl alcohol and extracted with ether. The residue from the ether yielded crystals, which, after draining, melted at about 40°, but owing to their tendency to liquefy under all solvents in which they were not extremely soluble, they were not recrystallised (Found : C, 73·0; H, 6·4. C_9H_9ON requires C, 73·4; H, 6·1%). The constitution of the substance was established by the observations (i) that, on boiling with concentrated hydrochloric acid, it yields phthalimidine, (ii) that, on heating in an open tube until visible decomposition commences, *N*-methylphthalimidine (XVI) is produced. The latter substance was isolated by crystallisation from ether and identified by direct comparison with a specimen prepared by the reduction of *N*-methylphthalimide.

*Oxidation of Methoxy*isoindole-2-*oxide to Phthalimide.*—This oxidation was carried out like that described on p. 1705, using, however, sufficient permanganate to supply rather more than four atoms of oxygen. On working up the product, phthalimide was obtained and identified in the usual way.

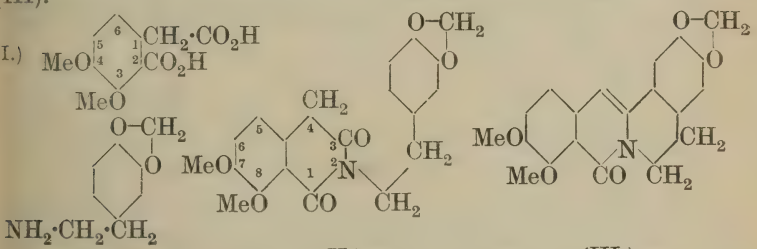
The authors desire to thank the Chemical Society for a grant with the aid of which the expenses of this investigation have been met.

Imperial College, South Kensington.
The University, Leeds. [*Received, April 20th,* 1925.]

CCXXVIII.—*Synthetical Experiments in the* iso-*Quinoline Group. Part V. Synthesis of Substances allied to Oxyberberine.*

By Robert Downs Haworth, William Henry Perkin, jun., and Herbert Sheppard Pink.

During the course of these synthetical experiments in the group of the berberine alkaloids, it was thought probable that 3 : 4-dimethoxyhomophthalic acid (I) would condense with homopiperonylamine (Ia) with the formation of 2-*homopiperonyl*-7 : 8-*dimethoxyhomophthalimide* (II) and that this substance, under the influence of a suitable dehydrating agent, might yield oxyberberine (III).



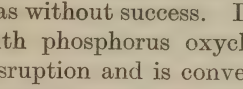
(I.) (Ia.) (II.) (III.)

This plan is independent of, but on similar lines to, the successful synthesis of oxyberberine by Perkin, Ray, and Robinson (this vol., p. 740) and as we have now succeeded with its aid in preparing several substances allied to oxyberberine, there can be little doubt that, when it is extended, it will ultimately lead to the synthesis not only of oxyberberine but also of oxypalmatine and allied substances and therefore indirectly to the synthesis of the corresponding alkaloids. The 3 : 4-dimethoxyhomophthalic acid required for the suggested synthesis was unknown and, while we were working out a method for its preparation, we decided to carry out a preliminary investigation with homophthalic acid itself and with 4 : 5-dimethoxyhomophthalic acid, both of which were available.

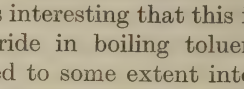
Homophthalic acid may be made from phthalide and potassium cyanide (Wislicenus, *Annalen*, 1886, **233**, 102), a method which, owing to the difficulty in controlling the temperature of interaction, can only be used on a small scale. It may also be prepared by the action of phosphorus pentachloride on 2-*iso*nitroso-1-hydrindone, as described by Perkin and Robinson (J., 1907, **91**, 1073), but the best method is that recommended by Ingold and Piggott (J., 1923, **123**, 1483), namely, from 1-hydrindone by oxidation.

Homophthalic acid condenses readily with β-phenylethylamine

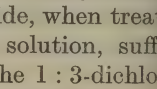
to give 2-β-*phenylethylhomophthalimide* (IV), which dissolves i alkali to a yellow solution with a green fluorescence and condens with aldehydes at the $-CH_2 \cdot CO-$ group. When treated with methy iodide and sodium hydroxide, it yields the 4 : 4-*dimethyl* derivativ (V) and all attempts to obtain the monomethyl derivative, whic would have been useful in the synthesis of substances of the coryd aline type, were unfortunately unsuccessful. A series of experi ments, made with the object of converting this imide into th parent of oxyberberine (X, oxyprotoberberine, compare this vol. p. 1462) by the action of dehydrating agents such as hydroge chloride, thionyl chloride, phosphorus pentoxide or oxychloride was without success. It is interesting that this imide, when treate with phosphorus oxychloride in boiling toluene solution, suffer disruption and is converted to some extent into the 1 : 3-dichloro *iso*quinoline (VI) described by Gabriel (*Ber.*, 1886, **19**, 1655).



(IV.)



(V.)

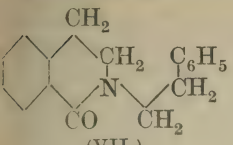


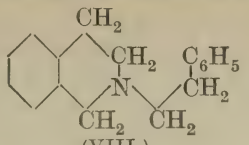
(VI.)

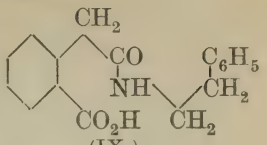
The stability of the imide (IV) to dehydrating agents is probably due to the carbonyl group in the 1-position in the *iso*quinoline ring and attempts were made to reduce this group without reducing the carbonyl group in the 3-position. It was found that zinc dust and sodium amalgam have no action on alkaline solutions of the imide under mild conditions and that, under vigorous conditions, it slowly undergoes hydrolysis. The imide may, however, be reduced electrolytically to a mixture of 2-β-*phenylethyl*-3 : 4-*dihydro*-1-iso*quinolone* (VII) and 2-β-*phenylethyl*-1 : 2 : 3 : 4-*tetrahydro*iso-*quinoline* (VIII). The former is insoluble in alkali, does not condense with aldehydes or suffer internal condensation when it is treated with phosphorus oxychloride, and cannot therefore be the isomeric 3-*iso*quinolone. It is clearly the carbonyl group in the 3-position in the imide which is the more readily reducible and, so far, it has not been found possible to leave this intact and reduce the group in the 1-position. Experiments are, however, in progress with the object of preparing the 3-keto-derivative synthetically.

When the imide (IV) is heated for several hours with sodium hydroxide, the yellow colour gradually disappears and an N-β-*phenylethylhomophthalamic acid* is produced which probably has structure (IX), but direct evidence of this view of its constitution is not yet available (compare, however, Gabriel and Posner, *Ber.*, 1894, **27**, 2504).

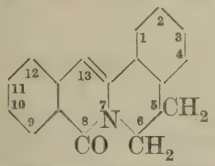
Further experiments on this point are in progress.

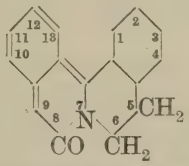

(VII.)


(VIII.)

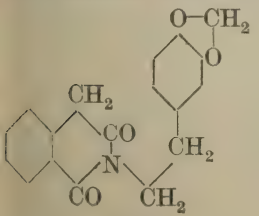

(IX.)

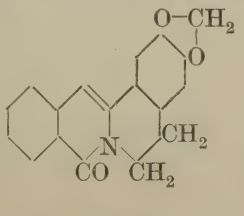
The *methyl* ester of the acid (IX) yields, on treatment with phosphorus oxychloride, a small quantity of a substance (m. p. 234°) which has the composition, $C_{17}H_{13}ON$, of oxyprotoberberine (X). The bright yellow colour of this substance is, however, not in accord with this structure and we are of the opinion that it is the *oxy*iso*protoberberine* of the formula (XI; compare XVIII), but the detailed investigation of this substance was rendered difficult on account of the small yield obtained.

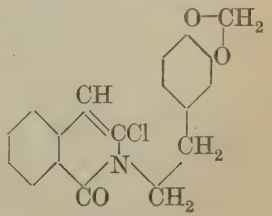
(X.) 


(XI.)

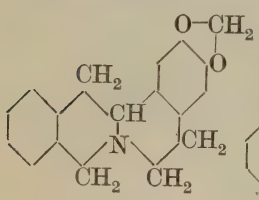
It is well known that derivatives of *iso*quinoline are formed with difficulty from unsubstituted β-phenylethylamine derivatives and that ring closure is much facilitated by the introduction of methoxy- or methylenedioxy-groups. With the view of obtaining increased yields of substances similar to those just described, a series of experiments was next carried out using homopiperonylamine (Ia) in the place of β-phenylethylamine, and 2-*homopiperonylhomophthalimide* (XII) was readily obtained by condensing this with homophthalic acid. It is curious that this imide could not be converted into a substance of the oxyberberine type (XIII) by the action of dehydrating agents and also that, while the imide (IV) yields 1 : 3-dichloro*iso*quinoline (VI) on treatment with phosphorus oxychloride, the imide (XII) does not suffer disruption under these conditions but is converted into 3-*chloro*-2-*homopiperonyl*-1-iso*quinolone* (XIV). Attempts to convert this chloro-derivative into the substance (XIII) by treatment with copper powder and quinoline were unsuccessful.


(XII.)

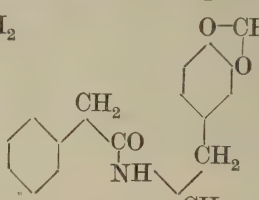

(XIII.)


(XIV.)

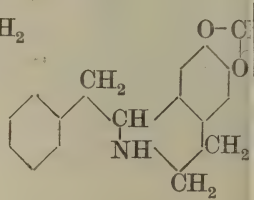
The imide (XII) is converted into the corresponding N-β-*hom*
piperonylhomophthalamic acid (compare IX) on warming with alk
and the investigation of the action of phosphorus oxychloride on
methyl ester of this acid has given interesting results. Two s
stances, *A* and *B*, are produced and of these, *A* (m. p. 180°)
colourless, feebly basic substance, has all the properties to
expected of 2 : 3-*methylenedioxyoxyprotoberberine* (XIII). It m
be reduced electrolytically to the corresponding 2 : 3-*methyle*
dioxytetrahydroprotoberberine (XV, m. p. 129°).



(XV.)



(XVI.)

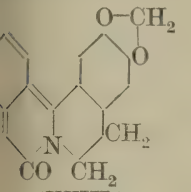


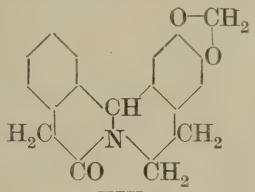
(XVII.)

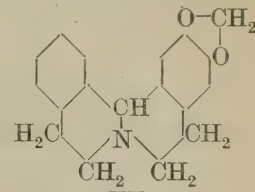
The correctness of the expression (XIII) for the substance *A* receiv
confirmation from the following independent synthetical expe
ments. *N*-Phenylacetylhomopiperonylamine (XVI), prepared
the method described by Decker (*Annalen*, 1913, **395**, 294), w
converted, by treatment with phosphorus oxychloride, into 6 :
methylenedioxy-1-*benzyl*-3 : 4-*dihydro*isoquinoline, and this reduc
to 1-*benzyl*nor*hydrohydrastinine* (XVII). This base, owing doubtle
to the absence of methoxy-groups in the ring, does not condense wi
formaldehyde and hydrochloric acid, and heating with formaldehy
and formic acid in a sealed tube leads exclusively to the formation
the N-*methyl* derivative (benzylhydrohydrastinine, p. 1721). Whe
however, the *N*-formyl derivative of the base (XVII) is treated wi
phosphorus oxychloride, it yields 2 : 3-*methylenedioxydihydroprotobe*
berine and this, on reduction, is converted into the tetrahydr
derivative, which melts at 129° and is identical with the substan
(XV) produced by the reduction of *A*. Consequently, *A* mu
have the constitution (XIII).* The second substance, *B*, produce
by the action of phosphorus oxychloride on the methyl ester
N-β-homopiperonylhomophthalamic acid (see above), has properti
similar to those of oxy*iso*protoberberine (XI) and it is suggeste
that it is 2 : 3-*methylenedioxyoxy*iso*protoberberine* (XVIII). It is

* If further evidence is required, it is supplied by the fact that 2 :
methylenedioxytetrahydroprotoberberine, on treatment with iodine followe
by silver chloride, yields the corresponding protoberberinium chloride, whic
is decomposed by alkalis, in the same manner as ordinary berberinium chlorid
yielding 2 : 3-methylenedioxydihydroprotoberberine and 2 : 3-methylened
oxyoxyprotoberberine, the latter being identical with *A* (compare p. 1723).

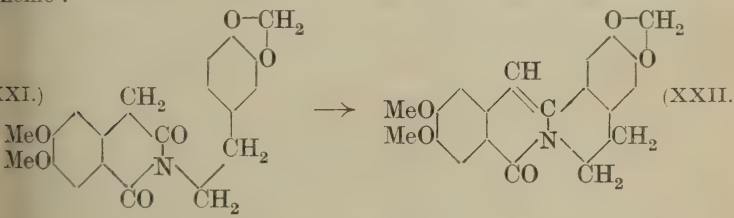
arlet, crystalline substance (m. p. 225°), dissolving with difficulty hydrolytic solvents, from which it separates in the hydrated form orange needles which lose weight at 100° and are converted into ie scarlet, anhydrous substance. On electrolytic reduction, the arlet substance is first converted into the colourless 2 : 3-*methylene*-*oxyoxydihydro*iso*protoberberine* (XIX) and then into 2 : 3-*methylene*-*oxytetrahydro*iso*protoberberine* (XX) isomeric with the substance XV).


(XVIII.)


(XIX.)


(XX.)

Synthesis of Oxy-ψ-berberine (compare Haworth, Perkin, and ankin, J., 1924, **125**, 1691).—This synthesis, indicated by the heme :

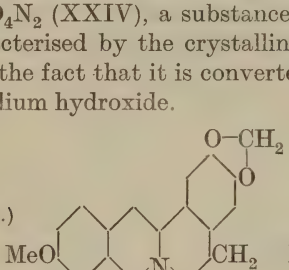

(XXI.) (XXII.)

as carried out in the following manner. 2-*Homopiperonyl*-6 : 7-*methoxyhomophthalimide* (XXI), prepared from 4 : 5-dimethoxy-omophthalic acid and homopiperonylamine, was converted, by ydrolysis with alkali, into the corresponding amic acid (compare X). When the *methyl* ester of this acid was treated with phos-horus oxychloride, it gave a 70% yield of a substance melting at 8° which was identical with the oxy-ψ-berberine described by aworth, Perkin, and Rankin. It is interesting that no isomeride this substance could be detected in the product of the interaction the methyl ester with phosphorus oxychloride. The imide XXI), on treatment with phosphorus oxychloride, behaves similarly 2-homopiperonylhomophthalimide (XII), yielding 3-*chloro*-2-*mopiperonyl*-6 : 7-*dimethoxy*-1-iso*quinolone* (compare XIV).

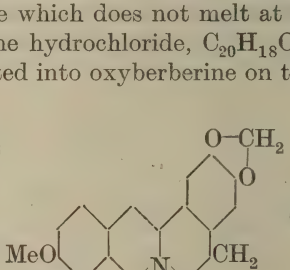
At the commencement of this research it became necessary to termine whether substances of the oxyberberine type are stable wards phosphorus oxychloride, that is to say, whether they are pable of formation in the presence of this reagent. Experiment owed that oxyberberine is readily acted on by phosphorus oxy-

chloride, two substances being formed, namely, methyl*nor*ox berberine (Faltis, *Monatsh.*, 1910, **31**, 573; Bland, Perkin, a Robinson, J., 1912, **101**, 262; compare this vol., p. 744) and chloro-derivative which clearly has the constitution (XXII because, when treated with ammonia, it yields *iminoberer* $C_{20}H_{18}O_4N_2$ (XXIV), a substance which does not melt at 280° a is characterised by the crystalline hydrochloride, $C_{20}H_{18}O_4N_2,H($ and by the fact that it is converted into oxyberberine on treatme with sodium hydroxide.

(XXIII.)



(XXIV.)



During the synthesis of oxy-ψ-berberine described above, crystalline chloro-derivative was also obtained in small quanti which, since it yielded oxy-ψ-berberine on treatment with sodiu hydroxide, was clearly the derivative corresponding to (XXIII).

Experimental.

β-*Phenylethylamine*.—β-Phenylpropionamide was prepared the following method, which gives good results and does not seem have been previously described. β-Phenylpropionyl chloride (p pared by boiling phenylpropionic acid with a slight excess of thion chloride and distilling the product under reduced pressure), d solved in dry benzene, is saturated with dry ammonia, and t mixture of ammonium chloride and the amide recrystallised fro hot water with the aid of animal charcoal. The amide separat in colourless leaflets (m. p. 105°) and is sufficiently pure for co version into β-phenylethylamine by means of sodium hypochlori (Decker, *Annalen*, 1913, **395**, 291).

β-3 : 4-*Dimethoxyphenylpropionic Acid*.—Veratraldehyde (100 g malonic acid (130 g.), and piperidine (5 c.c.) were heated in pyridi solution (250 c.c.) for 1½ hours on the steam-bath, during whi rapid elimination of carbon dioxide took place, and the reaction w completed by boiling for 10 minutes. The product, on pouring in excess of dilute hydrochloric acid, gave an almost quantitati yield of 3 : 4-dimethoxycinnamic acid, which was reduced to 3 : dimethoxyphenylpropionic acid by sodium amalgam under t conditions described by Perkin and Robinson (J., 1907, 9 1079).

2-β-*Phenylethylhomophthalimide* (IV).—β-Phenylethylamine ydrochloride (15·6 g.) is dissolved in water, the base liberated with otassium hydroxide, extracted with benzene, dried over potassium ydroxide, mixed with homophthalic acid (18 g.), and heated in an il-bath at 180° for 3 hours. The product is dissolved in boiling lcohol and cooled, when the *imide* (IV) separates in almost colour-ss prisms (19 g.) and is sufficiently pure for most purposes. After second crystallisation from alcohol, it was obtained in colourless risms, m. p. 128—129° (Found: C, 77·0; H, 5·8. $C_{17}H_{15}O_2N$ equires C, 77·0; H, 5·7%).

2-β-Phenylethylhomophthalimide (IV) is insoluble in water, paringly soluble in ether, and readily soluble in hot alcohol or cetic acid. It dissolves in sodium hydroxide to a yellow solution ith a green fluorescence and is reprecipitated by saturation with arbon dioxide. If, however, the alkaline solution is warmed for veral hours, the colour disappears and the imide is no longer recipitated by carbon dioxide.

The imide (1 g.) was heated in a sealed tube with phosphorus xychloride (3 c.c.) at 140—150° for 3 hours, the excess of oxy-hloride removed by distillation under reduced pressure, the residue ixed with sodium hydroxide, and the solid collected. This ubstance crystallised from methyl alcohol containing animal harcoal in colourless needles (m. p. 123°) and was evidently identical ith the 1 : 3-dichloro*iso*quinoline (VI) obtained by Gabriel (*loc. cit.*) Found: C, 54·8; H, 2·6. Calc., C, 54·5; H, 2·5%).

2-β-*Phenylethyl*-4 : 4-*dimethylhomophthalimide* (V).—2-β-Phenyl-hylhomophthalimide (2 g.) was dissolved in a solution of sodium ·35 g.) in alcohol (7 c.c.) and water (10·5 c.c.), methyl iodide (3 g.) dded, and the mixture gently boiled until the green fluorescence ad disappeared. Some of the alcohol was removed by distillation, he residue mixed with water, the precipitated oil extracted with her, the extract dried over anhydrous magnesium sulphate, aporated, and the oil distilled under 10 mm., when a colourless stillate was obtained which solidified on prolonged rubbing ith petroleum (Found: C, 77·7; H, 6·5. $C_{19}H_{19}O_2N$ requires 77·8; H, 6·5%). This dimethyl derivative crystallises from queous alcohol in colourless needles (m. p. 60—61°) and is readily luble in ether, but sparingly soluble in petroleum and insoluble sodium hydroxide. That the methyl groups in (V) are both tached to carbon is shown by the fact that no methyl iodide is tained when the substance is boiled with hydriodic acid.

2-β-*Phenylethyl*-3 : 4-*dihydro*-1-iso*quinolone* (VII). 2-β-Phenyl-hylhomophthalimide (2 g.), dissolved in a mixture of alcohol 0 c.c.) and concentrated sulphuric acid (40 c.c.), was placed in the

cathode compartment of an electrolytic cell, the cathode of which consisted of a piece of lead (150 sq. cm. surface) and the anode of a sheet of lead surrounded by sulphuric acid (20%). After a current of 5 amperes had been passed for 16 hours, the solution was diluted with water, extracted with chloroform, the extract dried over potassium carbonate, the solvent removed, and the residue crystallised from ether–petroleum (b. p. 40—60°), separating in colourless needles, m. p. 77—78° (Found: C, 81·3; H, 7·0. $C_{17}H_{17}ON$ requires C, 81·3; H, 6·8%). 2-β-*Phenylethyldihydroisoquinolone* is very soluble in organic solvents with the exception of petroleum, insoluble in dilute acids or alkalis, and will not condense with aldehydes in the presence of sodium ethoxide or piperidine.

2-β-*Phenylethyl*-1 : 2 : 3 : 4-*tetrahydroisoquinoline* (VIII).—The acid mother liquors from the preparation of the *iso*quinolone (see above) were made strongly alkaline with sodium hydroxide, extracted with chloroform, the extract dried over potassium carbonate, and the chloroform removed, when a basic oil remained which did not crystallise. This dissolved completely in dilute hydrochloric acid and, on concentrating, the *hydrochloride* crystallised; it separated from alcohol–ether in long, colourless needles, m. p. 227—229° (Found: C, 74·8; H, 7·4. $C_{17}H_{19}N,HCl$ requires C, 74·6; H, 7·3%).

N-β-*Phenylethylhomophthalamic Acid* (IX).—2-β-Phenylethyl homophthalimide (1·3 g.) was heated with *N*-sodium hydroxide (10 c.c.) for 12 hours on the steam-bath, when the imide dissolved and the yellow colour of the solution gradually disappeared. After cooling, the unchanged imide was precipitated by carbon dioxide and the filtrate acidified with concentrated hydrochloric acid; the straw-coloured gum, which soon hardened, crystallised from benzene in colourless needles, m. p. 122—123° (Found: C, 72·2; H, 5·9 $C_{17}H_{17}O_3N$ requires C, 72·1; H, 6·0%). This acid is readily soluble in alcohol, ether, or benzene, sparingly soluble in water or petroleum and dissolves in sodium bicarbonate with effervescence.

The *methyl* ester. When a methyl-alcoholic solution of the acid is saturated with dry hydrogen chloride, only a small yield of the methyl ester is obtained, the main product being the imide (IV), but the methyl ester may be obtained in a yield of 60% in the following way. The amic acid (2·8 g.), dissolved in a solution of sodium carbonate (0·53 g.) in water (50 c.c.), is mixed with a strong solution of silver nitrate (1·7 g.) and, after remaining for 2 hours in the dark, the silver salt is collected and thoroughly dried in a vacuum desiccator over sulphuric acid. The powdered salt, suspended in dry ether, is boiled under reflux with methyl iodide (2 g.) for 8 hours, and the solution is filtered and concentrated

when the *methyl* ester separates in colourless prisms, m. p. 74—75° (Found : C, 72·9 ; H, 6·5. $C_{18}H_{19}O_3N$ requires C, 72·7 ; H, 6·4%).

*Oxy*iso*protoberberine* (XI).—The above methyl ester (1 g.) was boiled with phosphorus oxychloride (2 c.c.) and toluene (5 c.c.) for an hour, hydrogen chloride being evolved and a brown gum separating. The product was diluted with petroleum (b. p. 40—60° ; 100 c.c.), the clear liquid, which contained considerable quantities of the imide (IV), decanted, the brown gum dissolved in alcohol, mixed with sodium hydroxide, and the dark insoluble substance collected. It separated from glacial acetic acid in yellow needles, m. p. 234° (Found : C, 83·3 ; H, 5·2. $C_{17}H_{13}ON$ requires C, 82·6 ; H, 5·3%). *Oxy*iso*protoberberine* is a weak base, dissolving in strong acids and being reprecipitated on dilution with water. It is sparingly soluble in organic solvents and its solutions in alcohol and glacial acetic acid exhibit an intense green fluorescence. The yield of this substance under the most favourable conditions is very small and in many experiments it could not be isolated at all.

2-*Homopiperonylhomophthalimide* (XII).—Homopiperonylamine was heated with homophthalic acid under conditions similar to those already described in the preparation of the imide (IV ; p. 1715). The product separates from alcohol or glacial acetic acid in colourless needles, m. p. 156—157°, is insoluble in water, but dissolves in warm potassium hydroxide to a yellow solution with a green fluorescence which becomes gradually colourless on boiling (Found : C, 69·9 ; H, 4·8. $C_{18}H_{15}O_4N$ requires C, 69·9 ; H, 4·8%).

2-*Homopiperonyl*-4 : 4-*dimethylhomophthalimide* (compare V) was prepared as described on p. 1715 and on pouring into water, a crystalline precipitate separated which crystallised from methyl alcohol, in which it was sparingly soluble, in long, pale yellow, rectangular prisms, m. p. 126—127°. It is insoluble in aqueous alkali and could not be hydrolysed to the corresponding homophthalamic acid (Found : C, 71·3 ; H, 5·8. $C_{20}H_{19}O_4N$ requires C, 71·2 ; H, 5·6%).

3-*Chloro*-2-*homopiperonyl*-1-iso*quinolone* (XIV).—The imide (XII, 1 g.) was boiled with a mixture of phosphorus oxychloride (3 c.c.) and toluene (10 c.c.) for 6 hours, during which hydrogen chloride was evolved, and, on cooling, a brown syrup separated. After dilution with petroleum (b. p. 40—60°), the clear liquid (which contained unchanged imide and some chloro-derivative) was decanted and the residual oil dissolved in a little alcohol. Sodium hydroxide was then added to remove unchanged imide, and the insoluble solid collected and recrystallised from methyl alcohol, from which it separated in short needles, m. p. 128—129° (Found : C, 66·4 ; H, 4·3. $C_{18}H_{14}O_3NCl$ requires C, 66·1 ; H, 4·3%). When

this chloro-derivative was heated with copper powder in boili quinoline solution and the quinoline removed by dilute hydrochlor acid, no trace of a condensation product could be isolated.

N-*Homopiperonylhomophthalamic Acid* (compare IX).—This ac was obtained from the imide (XII) by heating with *N*-sodiu hydroxide (2 mols.) for 12 hours on the steam-bath. After saturatio with carbon dioxide to remove unchanged imide, the filtered sol tion was acidified with concentrated hydrochloric acid, when yellow gum separated which soon hardened, and crystallised fro dilute acetic acid (1 : 1) in needles, m. p. 158—159° (Found : C, 66· H, 5·0. $C_{18}H_{17}O_5N$ requires C, 66·0; H, 5·2%). The *methyl* est was prepared by the esterification of the acid with methyl alcoh and hydrogen chloride and also by the action of methyl iodide o the silver salt (compare p. 1716). It crystallises with difficulty a then separates from ether in long, colourless needles, m. p. 95—9 (Found : C, 67·1; H, 5·6. $C_{19}H_{19}O_5N$ requires C, 66·9; H, 5·5%

The *amide* was prepared by dissolving the ester in ten times i weight of methyl alcohol and saturating with dry ammonia. Th solution turned green and white needles of the imide (XII) separate on diluting the filtrate with water, the amide was deposited as crystalline mass, which separated from dilute methyl alcohol needles, m. p. 216° (Found : N, 8·7. $C_{18}H_{18}O_4N_2$ requires 8·6%).

2 : 3-*Methylenedioxyoxyprotoberberine* (XIII).—The above meth ester (3 g.), phosphorus oxychloride (6 c.c.), and toluene (15 c.c were boiled for an hour, cooled, diluted with petroleum (b. p. 40- 60°), and the solvents (which contained the imide XII and some the chloro-derivative XIV) decanted from the gum. The latt was extracted with boiling dilute hydrochloric acid, the insolub portion dissolved in hot methyl alcohol and cooled, when a ma of almost colourless needles separated; a further quantity separate in fine needles on concentrating the acid extract, the filtrate fro which contained the substance XVIII (see below). 2 : 3-*Methylen dioxyoxyprotoberberine* separates from methyl alcohol in colourle needles, m. p. 180°, and is sparingly soluble in ether, benzene, cold alcohol, but readily soluble in hot alcohol or glacial acetic aci It dissolves in concentrated mineral acids, but is reprecipitated dilution with water (Found : C, 74·3; H, 4·6. $C_{18}H_{13}O_3N$ requir C, 74·2; H, 4·5%).

2 : 3-*Methylenedioxytetrahydroprotoberberine* (XV).—The su stance XIII (1·5 g.), dissolved in alcohol (60 c.c.) and concentrate sulphuric acid (40 c.c.), was subjected to a current of 5 amperes f 20 hours in the cell described on p. 1716. The mixture was poure into water and extracted with chloroform, when some unchange

XIII separated. The acid filtrate from this was made strongly alkaline with ammonia, extracted with chloroform, the extract dried over potassium carbonate, and the solvent removed, when a brown, syrupy base remained which yielded a sparingly soluble *hydrochloride*, crystallising from water in prisms, m. p. 270° (decomp.). The *base*, liberated from the hydrochloride by sodium hydroxide, separated from methyl alcohol in colourless needles, m. p. 128—129° (Found : C, 77·2; H, 6·1. $C_{18}H_{17}O_2N$ requires C, 77·4; H, 6·1%). The *picrate*, prepared in alcoholic solution, crystallises from alcohol in yellow needles, m. p. 208—210° (decomp.).

2 : 3-*Methylenedioxyoxy*iso*protoberberine* (XVIII).—This highly coloured substance is contained in the acid mother-liquors obtained during the preparation of the substance XIII (see above). The liquors were evaporated and the residue was dissolved in glacial acetic acid containing a little acetic anhydride, when, after some time, a crystalline mass separated which was collected and boiled with water. The substance crystallises from dilute acetic acid in long, orange needles, which lose weight and become scarlet on drying on the steam-bath (compare p. 1713) ; m. p. 225—226° (Found : C, 74·5, 74·2 ; H, 4·8, 4·6. $C_{18}H_{13}O_3N$ requires C, 74·2 ; H, 4·5%). This substance is very sparingly soluble in alcohol, ether, or benzene, readily soluble in glacial acetic acid, and slightly soluble in water to a yellow solution. It is soluble in hot mineral acids, separating on cooling in orange needles which become scarlet on heating. The *acetate* separates from glacial acetic acid in pale yellow needles, m. p. 250° (decomp.), and is rapidly dissociated by water.

2 : 3-*Methylenedioxyoxydihydro*iso*protoberberine* (XIX).—This substance was obtained when 2 : 3-methylenedioxyoxy*iso*protoberberine (XVIII) (1 g.), dissolved in a mixture of alcohol (60 c.c.) and concentrated sulphuric acid (40 c.c.), was reduced with a current of 5 amperes in the cell described on p. 1716. The original orange solution became almost colourless and, after pouring into water, this was extracted with chloroform (B), the extract dried over potassium carbonate, and the solvent removed, when a brown syrup remained which crystallised from alcohol in nodules, m. p. 196—197°, and from dilute acetic acid in needles, m. p. 203—204° (Found : C, 73·7 ; H, 5·2. $C_{18}H_{15}O_3N$ requires C, 73·7 ; H, 5·1%). This dihydro-derivative is sparingly soluble in the usual organic solvents, dissolves in concentrated mineral acids, and is reprecipitated by water.

2 : 3-*Methylenedioxytetrahydro*iso*protoberberine* (XX).—The aqueous mother-liquors (B) from the chloroform extraction (see above) were made alkaline with ammonia and again extracted with chloroform, when a small amount of a basic substance was isolated. The yield of this substance was increased by continuing the above

reduction for 48 hours. The base is a syrup very soluble in organic solvents and has not been obtained in the crystalline state.

The *hydrochloride* is sparingly soluble and crystallises from dilute hydrochloric acid in small prisms decomposing at 260°. The *picrate*, prepared in methyl-alcoholic solution, crystallises from much methyl alcohol in long, yellow needles, m. p. 216—217° (Found: N, 11·2. $C_{24}H_{20}O_9N_4$ requires N, 11·0%).

2-*Homopiperonyl*-6 : 7-*dimethoxyhomophthalimide* (XXI).—This substance was prepared from homopiperonylamine and 4 : 5-dimethoxyhomophthalic acid as described on p. 1715 (Found: C, 65·0; H, 5·2. $C_{20}H_{19}O_6N$ requires C, 65·0; H, 5·1%). It is sparingly soluble in alcohol and crystallises from glacial acetic acid in pale yellow needles, m. p. 178—179°. It dissolves in warm sodium hydroxide to a yellow solution with a green fluorescence and is reprecipitated by carbon dioxide. The *dimethyl* derivative (compare V) was obtained by treating the imide with methyl iodide in alkaline solution under the conditions described on p. 1715. On pouring into water, a white solid separated which crystallised from methyl alcohol in colourless prisms, m. p. 151° (Found: C, 66·8; H, 5·9. $C_{22}H_{23}O_6N$ requires C, 66·5; H, 5·8%).

3-*Chloro*-2-*homopiperonyl*-6 : 7-*dimethoxy*-1-iso*quinolone* (compare XIV).—The above imide (1 g.) was heated with phosphorus oxychloride (2 c.c.) and toluene (5 c.c.) for 2 hours, during which hydrogen chloride was eliminated. Petroleum (b. p. 40—60°) was then added and, after standing for some time, the clear solution was decanted, the residue dissolved in alcohol, unchanged imide removed by treatment with sodium hydroxide, and the solid crystallised from glacial acetic acid, from which it separated in yellow needles, m. p. 163—164° (Found: C, 61·7; H, 4·7. $C_{20}H_{18}O_5NCl$ requires C, 61·9; H, 4·7%).

N-*Homopiperonyl*-4 : 5-*dimethoxyhomophthalamic Acid* (compare IX).—This was prepared by warming the imide with *N*-sodium hydroxide (2 mols.) for 12 hours on the steam-bath. On acidifying with concentrated hydrochloric acid, a grey, granular mass separated which crystallised from dilute acetic acid in needles, m. p. 181—182° (Found: C, 62·1; H, 5·5. $C_{20}H_{21}O_7N$ requires C, 62·0; H, 5·4%). The *methyl* ester, prepared by the two methods employed in the earlier cases (p. 1718), is sparingly soluble in ether and moderately soluble in methyl alcohol, from which it crystallises in colourless prisms, m. p. 136° (Found: C, 62·5; H, 5·6. $C_{21}H_{23}O_7N$ requires C, 62·8; H, 5·7%).

Oxy-ψ-berberine (XXII).—The above methyl ester (2 g.), phosphorus oxychloride (6 c.c.), and dry toluene (10 c.c.) were boiled for an hour, cooled, and diluted with petroleum (100 c.c.; b. p.

40—60°), and the clear solution decanted. The residue was washed with petroleum, digested with sodium hydroxide for 2 hours on the steam-bath, and the brittle solid boiled with a little alcoholic sodium hydroxide, collected, and crystallised from aqueous acetic acid, from which the substance separated in colourless needles, m. p. 267—268° (not depressed on admixture with a specimen of oxy-ψ-berberine prepared by Haworth, Perkin, and Rankin; *loc. cit.*). In several experiments a salt of the dichloro-derivative (compare XXIII) separated towards the end of the reaction as an orange-crystalline solid, which crystallised from methyl alcohol in orange-yellow needles, m. p. 204—205° (decomp.). It was soluble in water and, on treatment with sodium hydroxide and subsequent crystallisation from dilute acetic acid, gave oxy-ψ-berberine.

*Benzyl*nor*hydrohydrastinine* (XVII).—*N*-Phenylacetylhomopiperonylamine (XVI) (10 g.) was dissolved in toluene (50 c.c.) and boiled for 1½ hours with phosphorus oxychloride (20 c.c.). The solution was cooled, diluted with petroleum (b. p. 40—60°), the clear liquid decanted, the residual syrup dissolved in hot alcohol, acidified with sulphuric acid, and heated on the steam-bath with zinc dust until the intense blue fluorescence had disappeared. The solution was filtered hot, the zinc residues were thoroughly extracted with boiling water, and the base was liberated from the united filtrates by the addition of ammonia and extracted with benzene. The benzene extract was washed with water, dried over potassium hydroxide, and the benzene removed, when the residual syrup solidified to a pasty mass.

Benzyl*nor*hydrohydrastinine dissolves in the usual organic solvents with the exception of petroleum and crystallises from ether–petroleum in prisms, m. p. 64—66°. The *hydrochloride* separates from water in colourless, rectangular plates, m. p. 110°, and is sparingly soluble in water or alcohol and particularly sparingly soluble in dilute hydrochloric acid. The *picrate*, prepared in methyl-alcoholic solution, crystallises from methyl alcohol in short, thick prisms, m. p. 184—185° (Found: C, 55·3; H, 4·1. $C_{23}H_{20}O_9N_4$ requires C, 55·6; H, 4·0%). When the base was heated in methyl-alcoholic solution with formalin and diluted with water, an oil separated which was heated with hydrochloric acid, but no substance of the tetrahydroberberine type could be detected and the product contained large quantities of unchanged benzyl*nor*hydrohydrastinine hydrochloride.

Benzylhydrohydrastinine (p. 1712).—Benzyl*nor*hydrohydrastinine (XVII) (0·5 g.) was heated with water (5 c.c.), formic acid (1·2 c.c.), and formalin (1 g.) in a sealed tube for 8 hours at 180°. The product was diluted with water, made alkaline with sodium hydroxide, and

the solution decanted from the syrupy base. This was washed with water, and dissolved in hot dilute hydrochloric acid, when the *hydrochloride* of benzylhydrohydrastinine separated in colourless prisms, m. p. 174—175° (decomp.) (Found: C, 67·6; H, 6·2. $C_{18}H_{20}O_2NCl$ requires C, 68·0; H, 6·3%). The base, liberated from the hydrochloride, was a syrup which was not obtained in the crystalline state.

2 : 3 - *Methylenedioxydihydroprotoberberine*. — Benzyl*nor*hydrohydrastinine (5·4 g.) and anhydrous formic acid (1 g.) were heated in an oil-bath at 200° for 4 hours, the product dissolved in toluene (25 c.c.), and boiled with phosphorus oxychloride (10 c.c.) for 1½ hours. Light petroleum was added, the clear liquid decanted, the residue boiled with dilute hydrochloric acid and animal charcoal, filtered, and the filtrate concentrated, when clusters of yellow prisms of the hydrochloride separated. This was collected, dissolved in water, and the base liberated by sodium hydroxide as a pale yellow solid, which crystallised from ethyl alcohol in clusters of yellow needles, m. p. 128—129° (Found: C, 77·7; H, 5·5. $C_{18}H_{15}O_2N$ requires C, 77·9; H, 5·4%). The *hydrochloride* crystallises from dilute hydrochloric acid, in which it is sparingly soluble, in yellow prisms, m. p. 250°. The *picrate* separates from much alcohol or ethyl acetate in long, orange needles, m. p. 254—255°.

2 : 3-*Methylenedioxytetrahydroprotoberberine* (XV) was obtained by reducing the dihydro-derivative just described with zinc dust and sulphuric acid until the solution became colourless. The hot liquid was filtered, the filtrate decomposed by ammonia, the sticky base washed with water and crystallised from methyl alcohol, from which it separated in almost colourless needles, m. p. 128—129°. This base is identical with the substance resulting from the electrolytic reduction of 2 : 3-methylenedioxyoxyprotoberberine (XIII), since no depression in melting point was observed on mixing specimens which had been prepared by the two different methods.

The 2:3-*Methylenedioxyprotoberberinium Salts*.—The tetrahydro base (XV), dissolved in alcohol, was oxidised by means of iodine in the presence of sodium acetate, when a yellow, crystalline precipitate separated, and, after concentrating, the precipitate was collected, suspended in water, and sulphur dioxide passed. The *iodide* obtained, crystallised from much water in long, pale yellow needles which did not melt at 300° (Found: C, 53·8; H, 3·5. $C_{18}H_{14}O_2NI$ requires C, 53·6; H, 3·5%). The corresponding *chloride* was obtained by digesting the iodide with silver chloride in aqueous suspension for some hours, filtering, and concentrating the filtrate, when the chloride separated as bright yellow needles which did not melt at 250°. When this chloride was heated for ½ hour with 50%

potassium hydroxide, a semi-solid mass separated which hardened on cooling. It was collected, ground, and extracted with hot, very dilute hydrochloric acid. The acid solution, make alkaline with ammonia, yielded a base which crystallised from alcohol in clusters of pale yellow needles, m. p. 128—129°, and proved to be identical with the 2 : 3-methylenedioxydihydroprotoberberine which had been previously obtained (p. 1722) by another process. The substance insoluble in the dilute hydrochloric acid was crystallised from dilute acetic acid, when colourless needles were obtained which melted at 180° and were identical with the 2 : 3-methylenedioxyoxyprotoberberine (XIII) described on p. 1718.

The Action of Phosphorus Oxychloride on Oxyberberine.—Oxyberberine (10 g.) was boiled with phosphorus oxychloride (50 c.c.) for 6 hours, during which the solution became deep orange and a bulky precipitate separated; the excess of oxychloride was then removed by distillation and the solid heated with dilute hydrochloric acid and filtered. The residue crystallised from glacial acetic acid in small, colourless needles, m. p. 245°, and was identical with a specimen of methyl*nor*oxyberberine which had been prepared from oxyberberine by heating with hydrochloric acid in a sealed tube (compare p. 1713). The orange-coloured acid filtrate was decomposed with a large excess of concentrated ammonia, and the *iminoberberine* (XXIV) crystallised from much alcohol, from which it separated in small, pale yellow needles which did not melt at 280° (Found : C, 68·1; H, 5·0. $C_{20}H_{18}O_4N_2$ requires C, 68·6; H, 5·2%). It is sparingly soluble in organic solvents and, on warming with sodium hydroxide, ammonia is evolved and oxyberberine separates. The *hydrochloride* was prepared by dissolving the base in warm dilute hydrochloric acid and allowing to cool slowly, when orange plates separated which did not melt at 280° (Found : C, 61·6; H, 4·9; N, 7·0. $C_{20}H_{19}O_4N_2Cl$ requires C, 62·2; H, 5·0; N, 7·2%). This hydrochloride dissociates slowly in contact with moisture and is rapidly changed to oxyberberine on treatment with sodium hydroxide.

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CCXXIX.—*Researches on Sulphuryl Chloride. Part III. The Influence of Catalysts on the Chlorination of Toluene.*

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The present investigation on the chlorination of toluene was undertaken with the object of increasing our knowledge of the influence of catalysts on the chlorinating properties of sulphuryl chloride hitherto confined to the effect of the better known carriers on the chlorination of benzene (Silberrad, J., 1921, **119**, 2029; 1922, **121** 1015).

Previous investigators have recorded that no action occurs between toluene and sulphuryl chloride below 115° (Dubois, *Bull. Acad. Roy. Belg.*, 1872, 42), but that at that temperature benzyl chloride and chlorotoluene are slowly formed. Tohl and Eberhardt (*Ber.*, 1893, **26**, 2940), working at 160°, also obtained a mixture of these compounds, whilst Wohl (D.R.-PP. 1467/1902, 160102/1902 and 162394/1903) patented the manufacture of benzyl chloride (and its homologues) by heating toluene (and its homologues) with sulphuryl chloride to temperatures not exceeding 130°, the yield claimed in the absence of light being 50% on the toluene used. Tohl and Eberhardt (*loc. cit.*) also observed that iodine (at 160°) exercised no retarding influence on the formation of benzyl chloride, and Witte (*Pharm. Rec.* of New York, 1889, Dec. 16), Tohl and Eberhardt (*Ber.*, 1893, **26**, 2943), and Böeseken (*Rec. trav. chim.*, 1911, **30**, 381) obtained *o*- and *p*-toluenesulphonyl chloride as the chief product of treating toluene with sulphuryl chloride in the presence of aluminium chloride.

Apart from the simultaneous formation of chlorotoluene and benzyl chloride the present investigation has not confirmed these observations. The two ingredients react to a noticeable extent far below 115° in the absence of either light or catalysts, whilst iodine exercises a marked effect at 70° both by inhibiting side-chain substitution and by accelerating the formation of chlorotoluene. As regards the influence of aluminium chloride, toluenesulphonyl chloride or chlorotoluene can be produced at will according as the conditions selected are conducive to the Friedel and Crafts reaction or to chlorination; the former conditions appear to have been those selected by the above cited previous workers and the latter come within the present investigation (compare No. 3).

The catalysts examined may conveniently be divided into groups: those which either inhibit chlorination or alter its course without inducing any appreciable acceleration, and those which accelerate

substitution. Of the first series, phosphorus pentachloride is the most remarkable; it appears to prevent ring substitution altogether without, however, materially influencing the quantity of benzyl chloride produced in a given time.* Manganese chloride and arsenic also exhibit this peculiarity, though to a lesser extent, whilst the latter also accelerates side-chain substitution. All the other catalysts examined accelerate ring substitution and, with the exception of sulphur † and bromine, at the expense of the benzyl chloride produced, the yield of the latter compound being reduced to zero in the case of iron, aluminium, antimony, bismuth and tellurium.

Further, the catalytic activity of the elements of the same group, with the exception of bromine, is a function of the atomic weight, increasing with this apparently up to a maximum, as illustrated by bismuth (see table on p. 1726). In this respect, therefore, the elements examined behave in the same manner as halogen carriers in direct chlorination (Willgerodt, *J. pr. Chem.*, 1886, **33**, 264), from which it would appear that they operate as chlorine carriers rather than as dissociation catalysts. The only exception to Willgerodt's rule is furnished by bromine, which is much more active than iodine in spite of their relative atomic weights. It is suggested that this abnormality is due to the transient formation of sulphuryl bromide, concerning the existence of which there has been so much controversy (Odling, *Quart. J. Chem. Soc.*, 1854, **7**, 2; *Jahresbericht*, 1854, 308; *Handbuch Deutsch von Oppenheim*, 1865, **1**, 169; also Sestini, *Bull. Soc. chim.*, 1868, **10**, 226; Gustavson, *Ber.*, 1873, **6**, 9; Melsens, *Compt. rend.*, 1873, **76**, 92). This suggestion is borne out by the fact that bromine shows this abnormal activity only if previously dissolved in and added with the sulphuryl chloride and not when admixed with the hydrocarbon (Nos. 14 and 15), whereas with iodine, which admittedly shows no tendency to form sulphuryl iodide (compare Sestini, *loc. cit.*; Odling, *loc. cit.*), it makes but little difference whether it be added to the hydrocarbon or to the sulphuryl chloride (Nos. 16 and 17).

Not only is the intensity of the action a function of the atomic weight, but also the nature of the chlorination effected (see table); thus, the elements of the same group show a decreasing tendency to induce side-chain substitution with increasing atomic weight, but an increasing tendency to accelerate ring substitution. In all cases where the catalyst showed a marked influence the reaction was accompanied by the formation of strongly coloured inter-

* Erdmann (*Annalen*, 1893, **272**, 149), working with chlorine, found that phosphorus pentachloride accelerated side-chain substitution.

† This observation is in accord with Beck's work on the direct chlorination of toluene in the presence of sulphur (*Ber.*, 1892, **25**, 2445).

mediate products the constitution of which is evidently similar to those previously observed in the case of benzene, thus again contributing strong evidence in favour of the additive theory of chlorination (Silberrad, *loc. cit.*).

Comparative Action of Catalysts of the Same Periodic Group.

		Products obtained on boiling for 8 hours.				
Element.	At. wt.	% of chlorine in product.	% of chloro-toluene produced.	% of benzyl chloride produced.	Ratio chloro-toluene to benzyl chloride.	Coloration.
Group V.						
Phosphorus	31·04	2·1	nil	7·6	0·0	Nil
Arsenic ...	74·96	4·6	3·3	12·6	0·25	Amber
Antimony	120·2	26·2	93·1	nil	∞	Dark brown
Bismuth ...	208·0	21·1	76·4	nil	∞	Dark brown
Group VI.						
Sulphur ...	32·07	18·1	50·5	13·8	3·7	Pale amber
Selenium	79·2	23·2	77·0	5·2	14·8	Dark amber
Tellurium	127·5	25·1	89·1	nil	∞	Deep brown
Group VII.						
Bromine ...	79·92	10·8	26·9	11·3	1·3	—
Iodine	126·92	5·6	16·0	4·5	3·5	—

Experimental.

For the sake of brevity the method of procedure adopted is described in general terms and the quantitative results are summarised at the end of the paper, only peculiarities specific to each catalyst being described under that head. Unless stated otherwise, no coloration developed.

The apparatus and the method used were similar to those described by one of us (Silberrad, J., 1921, **119**, 2031), save that the mixture was boiled for 8 hours and light was found to produce so marked an effect on the results that its influence was rigidly excluded. The hydrocarbon (79 c.c. of toluene) was treated with 10% excess of sulphuryl chloride (66 c.c.) in the presence of the desired catalyst. The product was boiled with 250 c.c. of water * and steam-distilled, and the distillate dried and fractionated. The fraction boiling below 180° was freed from traces of dichloro-compounds by redistillation, and its composition then calculated from its density and the quantity of benzyl chloride present, estimated by boiling a weighed quantity with excess of solid silver nitrate and sufficient alcohol to form a boiling saturated solution (compare Schultze, *Ber.*, 1884, **17**, 1675; Cohen, Dawson, Blockey, and Woodmansey, J., 1910,

* Without this preliminary treatment sulphuryl chloride when present in any quantity passed over undecomposed on steam distillation.

97, 1625); a less concentrated solution of silver nitrate is liable to give inaccurate and erratic results.

No. 1. *Catalyst nil.*—The boiling ingredients slowly evolved sulphur dioxide and hydrogen chloride: the reaction was evidently not completed during the experiment (8 hours).

No. 2. *Catalyst Gold Chloride.*—Gold is apparently not attacked by sulphuryl chloride below about 150° (North, *Bull. Soc. chim.*, 1911, **9**, 646). It was therefore introduced as the anhydrous trichloride (1·3 g.). The velocity of chlorination was thereby raised about 30% without, however, appreciably altering the nature or relative proportion of the products. The reacting mixture assumed an amber tint.

No. 3. *Catalyst Aluminium Chloride* (*anhydrous*).—Aluminium chloride combines with sulphuryl chloride in the absence of moisture to form aluminium chlorosulphoxide, which acts as a powerful dissociation catalyst (Adrianowsky, *Ber.*, 1879, **12**, 688; Ruff, *Ber.*, 1902, **35**, 4453; *Chem. Ztg.*, 1906, **30**, 1225; Rohland, *Chem. Ztg.*, 1906, **30**, 1173; Silberrad, J., 1921, **119**, 2031). The anhydrous compound was therefore used, 14 g. being added to the toluene and the required quantity of sulphuryl chloride run into the mixture previously raised to 70°. A vigorous evolution of sulphur dioxide and hydrogen chloride took place at once and the reaction was completed in 2½ hours. The acceleration effected by this catalyst therefore amounted to approximately 1600%. The product, which was at first deep purple and finally dark vandyke-brown, had the characteristic odour of toluenesulphonyl chloride. The quantity was, however, small, chlorination being almost the only reaction under the above conditions.

No. 4. *Catalyst Carbon.*—Carbon is not attacked by sulphuryl chloride (Heinemann and Köchlin, *Ber.*, 1882, **15**, 1736; *Jahresbericht*, 1882, 234); any influence this substance might exercise was therefore likely to be physical rather than chemical. Finely-ground (200-mesh) wood charcoal was used (0·7 g.). A slight increase in the amount of nuclear substitution appeared to be induced.

No. 5. *Catalyst Stannic Chloride.*—Tin is only slowly attacked by sulphuryl chloride (Heinemann and Köchlin, *loc. cit.*), anhydrous stannic chloride (14 g.) was therefore used. Substitution took place almost entirely in the ring. The reacting products developed a faint pink tint.

No. 6. *Catalyst Phosphorus Pentachloride.*—In order to avoid complication arising from the possible formation of sulphur chloride *

* Sulphuryl chloride converts phosphorus into the trichloride (Köchlin and Heinemann, *Ber.*, 1881, **15**, 1736) and less readily into the pentachloride (North and Thompson, *J. Amer. Chem. Soc.*, 1918, **40**, 774), whilst the latter

the pentachloride (0·7 g.) was used. Chlorination proceeded even more slowly than without the catalyst, and the action was restricted entirely to side-chain substitution.

No. 7. *Catalyst Arsenic.*—Arsenic is rapidly converted into the trichloride by sulphuryl chloride (Köchlin and Heinemann, also Ruff, *loc. cit.*), The finely-ground element (0·7 g.) was therefore used. The reaction proceeded slowly, substitution occurring chiefly in the side chain.

No. 8. *Catalyst Antimony.*—Antimony reacts with sulphuryl chloride, forming the trichloride (Köchlin and Heinemann, *loc. cit.*). The element (0·7 g.) was therefore used. A steady and vigorous evolution of gas took place during the whole of the experiment, and the reaction was practically completed in 3 hours. The acceleration caused by this catalyst therefore amounted to 1300% approximately. The product, initially purple, gradually turned deep vandyke-brown. Substitution took place entirely in the ring.

No. 9. *Catalyst Bismuth.*—The action of sulphuryl chloride on this metal does not appear to have been previously examined. It dissolves readily, however, and was therefore introduced in the metallic form (0·7 g.). A vigorous action set in and a steady evolution of gas continued during the whole of the experiment. As a catalyst, bismuth behaves very similarly to antimony; the reaction mixture also passes through a precisely similar series of colour changes and substitution occurs wholly in the ring.

No. 10. *Catalyst Sulphur Chloride.*—According to Heinemann and Köchlin (*loc. cit.*) sulphuryl chloride does not act on sulphur at all; Ruff (*loc. cit.*), however, observed the formation of sulphur monochloride at 200°, and North and Thompson (*J. Amer. Chem. Soc.*, 1918, **40**, 774) observed it at 95—98°. Preliminary experiments with toluene showed that the hydrocarbon was very little attacked during the first 5 or 6 hours when elementary sulphur was used, but that after that the reaction proceeded just as rapidly as when sulphur chloride was added, thus proving beyond a doubt that sulphur is slowly converted into sulphur monochloride even at 70°. In order to avoid complication, therefore, the catalyst was intro-

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substance reacts with a further quantity of sulphuryl chloride with formation of thionyl chloride, phosphorus oxychloride, and chlorine (Michaelis, *Jenaische Z. Med. Naturwiss.*, 1871, **6**, 79; *Z. Chemie Pharm.*, von Beilstein Fittig u. Hubner, 1871, **6**, 460). The thionyl chloride reacts with a further quantity of phosphorus trichloride, producing phosphorus sulphur chloride (Michaelis, *Z. Chem. Pharm.*, von Beilstein Fittig u. Hubner, 1871, **6**, 151), which in its turn is reconverted into phosphorus pentachloride and sulphur chloride by a further quantity of sulphuryl chloride (Michaelis, *loc. cit.*; compare also North and Thompson, *loc. cit.*); hence the risk of complications through the formation of sulphur chloride.

luced in the form of sulphur chloride (0·7 g.). A steady and fairly trong reaction took place during the whole experiment, the amount f side-chain substitution being doubled and that in the ring quad-upled by this catalyst. The reacting liquid assumed a pale amber tint.

No. 11. *Catalyst Selenium.*—Selenium is rapidly attacked by ulphuryl chloride with formation of the tetrachloride (Lehner and North, *J. Amer. Chem. Soc.*, 1907, **29**, 33). The element (0·7 g.) was therefore used. A vigorous reaction proceeded throughout the experiment and the product assumed a dark amber colour.

No. 12. *Catalyst Tellurium.*—Tellurium is converted first into he di-, then into the tetra-chloride on heating with sulphuryl chloride Lenher, *J. Amer. Chem. Soc.*, 1898, **30**, 737). The element (0·7 g.) was therefore used. The reaction was perceptibly more vigorous han with selenium, chlorination being complete in 5 hours and substitution taking place almost entirely in the nucleus. The nixture, too, assumed a much darker tint, changing from a dull purple-brown in the early stages to a very dark amber-brown at he end.

No. 13. *Catalyst Manganese Chloride.*—The manganese was intro-luced as anhydrous iron-free manganous chloride, in the presence f which chlorination appeared to proceed even more slowly than without any addition.

No. 14. *Catalyst Bromine* (added to the hydrocarbon).—Sulph-ıryl chloride decomposes hydrogen bromide with liberation of romine, but then the reaction appears to stop (Besson, *Compt. end.*, 1896, **122**, 467). In conformity with this observation it was ound that bromine added to the hydrocarbon exercised little or io influence on the rate of chlorination.

No. 15. *Catalyst Bromine* (added to the sulphuryl chloride).—Having regard to the possibility of the intermediate formation of ulphuryl bromide, Experiment No. 14 was repeated, bromine being dded to the sulphuryl chloride instead of the hydrocarbon. The eaction was much more vigorous, approximately double the amount f substitution occurring in 8 hours.

No. 16. *Catalyst Iodine* (added to the hydrocarbon).—According o Ruff (*Ber.*, 1901, **34**, 1749) sulphuryl chloride alone is without ction on iodine. On prolonged boiling, however, a dilute solution f iodine in sulphuryl chloride became colourless, presumably due o the formation of iodine chloride. Added to the hydrocarbon, odine (0·7 g.) accelerated ring substitution to a small extent at the xpense of the benzyl chloride formed.

No. 17. *Catalyst Iodine* (added to sulphuryl chloride).—Unlike romine, iodine (0·7 g.) added to the sulphuryl chloride produced a

similar result to that obtained when the halogen was added to the hydrocarbon.

No. 18. *Catalyst Iron.*—According to North (*Bull. Soc. chim.*, 1911, **9**, 646), who obtained ferric chloride by heating iron with sulphuryl chloride to 160°, this metal is attacked by sulphuryl chloride with some difficulty. Heated in the presence of the hydrocarbon, however, it (0·7 g.) rapidly passed into solution and induced vigorous substitution in the nucleus. The reacting mixture assumed a dark olive-green colour.

No. 19. *Catalyst Platinum.*—According to North (*loc. cit.*) platinum behaves like iron when heated with sulphuryl chloride. The finely divided metal (0·7 g. of 20% platinum asbestos) was therefore used. The bulk of the platinum gradually passed into solution and exercised a slight accelerating influence.

TABLE.

Giving Quantitative Results obtained by boiling 0·75 *g.-mol. of Toluene with* 10% *excess Sulphuryl Chloride for* 8 *hours in the presence of Various Catalysts.*

		Products obtained.							
			Steam-distilled product.		Fractionated product.				
							Composition.		
No.	Catalyst.	Crude product. Yield c.c.	Yield c.c.	$d_{4^\circ}^{16^\circ}$.	Yield c.c.	$d_{4^\circ}^{16^\circ}$.	Toluene %.	Chloro-toluene %.	Benzyl chloride %.
1	Nil	80	73	0·921	60	0·905	80·3	12·8	6·9
2	Gold chloride	76	70	0·927	59	0·918	73·5	17·0	9·5
3	Aluminium chloride*	79	69	1·084	58·5	1·073	3·1	96·9	nil
4	Carbon	79	76	0·914	67·5	0·912	76·5	16·9	6·6
5	Stannic chloride ...	80	78	0·924	66·5	0·914	74·5	24·8	0·7
6	Phosphorus penta-chloride	80	77	0·900	62·5	0·880	92·4	nil	7·6
7	Arsenic	78	75	0·907	64·5	0·898	84·1	3·3	12·6
8	Antimony*	78	75	1·067	65·5	1·063	6·9	93·1	nil
9	Bismuth	80	78	1·027	63·2	1·022	23·6	76·4	nil
10	Sulphur chloride ...	79	76	1·010	62	0·997	35·7	50·5	13·8
11	Selenium	82	80	1·046	71	1·037	17·8	77·0	5·2
12	Tellurium*	80	79	1·069	71	1·053	10·9	89·1	trace
13	Manganese chloride	78	75	0·892	64·5	0·885	91·2	2·2	6·6
14	Bromine (added to hydrocarbon) ...	80	77	0·917	65	0·905	80·4	11·0	8·6
15	Bromine (added to SO_2Cl_2)	79	74	0·948	65·5	0·941	61·8	26·9	11·3
16	Iodine (added to hydrocarbon) ...	80	76	0·913	68·5	0·901	81·9	16·5	1·6
17	Iodine (added to SO_2Cl_2)	80	77	0·918	69·5	0·906	79·5	16·0	4·5
18	Iron	81	77	1·022	68	1·017	25·7	74·3	nil
19	Platinum	75	72	0·944	59	0·940	61·8	34·9	4·3

* In the presence of these catalysts the reaction was completed in less than 8 hours, namely, with aluminium chloride in 2½ hours, with antimony in 3 hours, and with tellurium in 5 hours.

ınks are due to Messrs. A. Boake Roberts & Co., Ltd., of , for supplying the sulphuryl chloride required for this ıtion.

ILBERRAD RESEARCH LABORATORIES,
UCKHURST HILL, ESSEX. [*Received, May 1st*, 1925.]

CCXXX.—*Stereoisomeric Azo-dyes.*

By GILBERT T. MORGAN and DONAL GEORGE SKINNER.

A STUDY of the absorption of asymmetric substances by animal fibres was made by Willstätter (*Ber.*, 1904, **37**, 2758), who employed racemoid alkaloids but without finding any preferential absorption of one optical component by wool or silk.

Porter and Hirst (*J. Amer. Chem. Soc.*, 1919, **41**, 1264) prepared a varied series of asymmetric azo-dyes with the object of establishing a definite relationship between the chemical structures of dyes and their function as vital stains. They report, but without giving practical details, one case of a racemoid dye on which wool acted selectively, absorbing more of the lævo- than of the dextrosomeride. Their azo-dyes, which contained an asymmetric carbon atom derived from *p*-aminobenzhydrol and the *p*-aminodiphenylalkylcarbinols, $NH_2 \cdot C_6H_4 \cdot CAlk(OH) \cdot C_6H_5$, were prepared by successively diazotising these amines and coupling the diazonium salt with β-naphthol, dimethylaniline, naphtholsulphonic acids, or naphthylaminesulphonic acids.

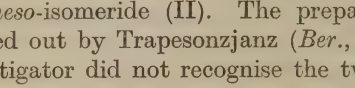
Ingersoll and Adams (*J. Amer. Chem. Soc.*, 1922, **44**, 2930) obtained *d*- and *l*-forms of *p*-aminobenzoyl-α-aminophenylacetic acid and converted these into two pairs of optically active dyes by diazotising and coupling with β-naphthol and dimethylaniline. The β-naphthol dyes were absorbed by wool in equal amounts, whereas the two dimethylaniline dyes were absorbed at unequal rates.

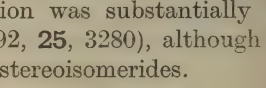
Racemoid aminomandelic acid was resolved by Porter and Ihrig through its cinchonine salt and its optically active components were diazotised and coupled with β-naphthol. When wool was dyed with a racemoid mixture of these azo-colouring matters, the dye-bath became lævorotatory owing to the higher rate of absorption of the dextro-form (*J. Amer. Chem. Soc.*, 1923, **45**, 1090).

In the experiments described below, two sets of stereoisomeric dyes were prepared and their enantiomorphous components were isolated.

n-Butyl alcohol, kindly supplied by Captain Desborough of the

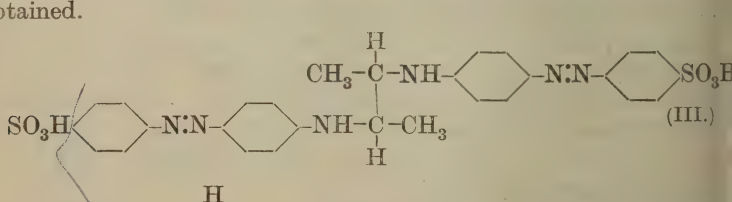
Royal Naval Cordite Factory, was converted successively into β-butylene and βγ-dibromo-*n*-butane. The last product was then condensed with aniline, whereby two stereoisomeric bases were obtained, but the *dl*-diamine (I) was in much larger yield than its *meso*-isomeride (II). The preparation was substantially that carried out by Trapesonzjanz (*Ber.*, 1892, **25**, 3280), although this investigator did not recognise the two stereoisomerides.

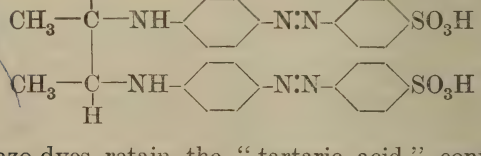
(I.) 


(II.)

Both stereoisomeric bases were oily, but of their solid derivatives it was found that those of the *meso*-diamine were less fusible and less soluble than those of the *dl*-isomeride.

The two diamines were separated by means of their crystallisable salts (nitrate, sulphate, picrate) and were coupled separately with diazotised sulphanilic acid, when two stereoisomeric azo-dyes were obtained.


(III.)


(IV.)

These disazo-dyes retain the "tartaric acid" configuration of the original bases. The compound IV from the *meso*-diamine was non-resolvable, whereas its isomeride III was resolved into optically active forms by means of the strychnine and cinchonidine salts.

The conditions under which solutions of the racemoid dye were kept in contact with wool for a prolonged interval at 20° were varied as to solvent, time of contact, and strength of solution, but only in one case was a slight optical activity observed in the dye-bath. The rates of absorption by wool of the four stereoisomeric dyes—the *dl*-, *d*-, *l*-, and *meso*-forms—were then investigated, and in all four cases the solutions of the dyes were of the same strength, the volume of the solution being proportional to

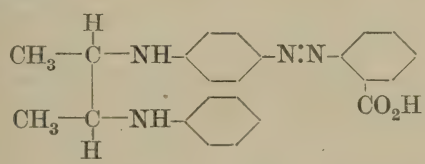
the weight of wool employed. At fixed intervals of time the amount of colouring matter remaining in solution was titrated by standard titanous chloride, this estimation giving a measure of the dye absorbed. The dextrorotatory dye was absorbed by the fibre at a slightly faster rate than the racemoid compound, whereas the lævorotatory isomeride was absorbed more slowly than either.

Although the differences in the measured rates of absorption of these three stereoisomeric forms were small, they were consistent for all the readings taken. The faster absorption of the *d*-compound was in agreement with the qualitative observation that a solution of the racemoid dye on prolonged contact with wool tended to become lævorotatory. The smallness of this optical activity had indicated that the differences in the rates of dyeing of the two enantiomorphs would also be small; the qualitative experiments confirm this anticipation and the greater rate of absorption of the *dextro*-form is also in agreement with the results of Porter and Ihrig (*loc. cit.*).

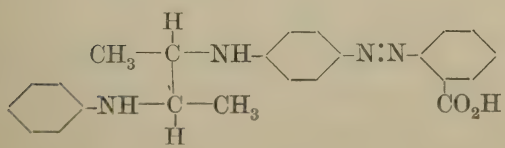
The *meso*-isomeride was found to dye wool at a much slower rate than any of its three stereoisomerides, this being the first case in which internally and externally compensated disazo-dyes have been contrasted.

Attempts were next made to demonstrate selective absorption by wool of less acidic colouring matters containing carboxyl groups and accordingly *dl*- and *meso*-diphenyl-βγ-diamino-*n*-butanes were coupled with diazotised anthranilic acid, when it was found that these diamines coupled with only one molecular proportion of the diazo-compound so that the resulting monoazo-dyes no longer retained any analogy with tartaric acid.

The *cis*- and *trans*-carboxyazo-dyes from the *meso*- and *dl*-diamines are represented respectively by formulæ V and VI, both being resolvable.



(V.)



(VI.)

Attempts were made with several alkaloids to resolve the latter more plentiful dye, dl-trans-2-*carboxybenzene*-4-*azodiphenyl*-βγ-*di*-

amino-n-*butane*, into its enantiomorphs, but only the lævorotatory isomeride was obtained and that through the agency of the strychnine salt.

The rates of absorption by wool of the three stereoisomerides when ascertained by the titanous chloride titration, showed that as in the case of the sulphonated disazo-dyes, the *lævo-trans*-compound was absorbed less readily than the *dl-trans*-isomeride, the differences being greater than those observed with the sulphonated dyes. The rates of absorption for the two racemoid, *cis*- and *trans*-carboxylated azo-dyes were practically identical.

Experimental.

Stereoisomeric Diphenyl-βγ-diamino-n-*butanes.*

The vapour of *n*-butyl alcohol was passed through a mixture of sand and phosphoric acid at 300—350° contained in a cylindrical copper vessel, and to the distillate of crude β-butylene, condensed and cooled with ice and salt, was added bromine drop by drop so that only a slight excess of halogen was present. The dibromide, washed with aqueous alkali and dried, was distilled fractionally until βγ-dibromo-*n*-butane was isolated, b. p. 157—158° (J., 1923, **123**, 97).

Aniline (600 g.) and 60 g. of βγ-dibromide were heated together at 160° for 4 hours, when the mixture became pasty owing to the separation of hydrobromides. After neutralisation with saturated aqueous sodium carbonate the mixture was distilled in steam to remove excess of aniline, and the residue extracted with benzene or ether. The crude diamines left on evaporating the solvent weighed 50 g. (yield 74%, calculated on βγ-dibromide).

dl-*Diphenyl-βγ-diamino*-n-*butane* (I).—The crude bases, consisting mainly of *dl*-diamine and a small proportion of *meso*-diamine, were dissolved in 50 c.c. of alcohol, 50 c.c. of nitric acid (*d* 1·42), and 100 c.c. of water, the solution being stirred and cooled in ice and salt. The crystalline *dl*-diamine nitrate which separated was recrystallised from alcohol until it melted with decomposition at 170—175° (weight 37 g.). The purified nitrate was decomposed with ammonia, the liberated base extracted with benzene and precipitated as picrate by adding picric acid (1 mol.) dissolved in the same solvent. The product was crystallised repeatedly from benzene until the purified *dl*-picrate melted at 136—137° (weight 36 g.). This method of purification depends on the fact that the small proportion of *meso*-diamine does not form a crystallisable picrate. Alternatively the *dl*-base may be purified by repeated crystallisation of its sulphate. This diamine, liberated by ammonia from its nitrate, was extracted with benzene, dissolved in alcohol,

and treated with the calculated amount of 30% sulphuric acid. The sulphate which separated was crystallised repeatedly from alcohol until a constant melting point—182°—was attained (Found: S, 9·4. $C_{16}H_{20}N_2,H_2SO_4$ requires S, 9·5%).

meso-*Diphenyl*-βγ-*diamino*-n-*butane* (II).—The *meso*-diamine, formed only in small amount by the condensation of βγ-dibromo-*n*-butane and aniline, is present together with *dl*-isomeride in the mother-liquors from the nitrate and picrate of the latter base. It was set free in the solutions by ammonia and extracted with benzene. The crude diamines obtained after concentrating the benzene extract weighed 21 g. and were converted into sulphate with 30% sulphuric acid, when the crystalline product obtained was *dl*-diamine sulphate. The filtrate was cooled and treated with dilute aqueous sodium nitrite; the viscid, brownish-yellow nitrosoamine was removed with ether and crystallised from petroleum (b. p. 80—100°) until it separated in pale yellow, arborescent growths of the purified *meso*-butylene-βγ-diphenyldinitrosoamine, m. p. 125°. A small amount of uncrystallisable oily residue was left consisting of the mixed *dl*- and *meso*-dinitrosoamines.

The dinitrosoamine was reduced with tin and hydrochloric acid in hot alcoholic solution, and the solution containing the stannichloride of the diamine was rendered alkaline with sodium hydroxide until the tin hydroxides redissolved. The oily diamine was extracted with benzene (yield 37%) and converted into its sulphate, which crystallised from alcohol and melted at 206°. This sulphate was not only less fusible but also less soluble in alcohol than the sulphate of the *dl*-diamine. The latter property was utilised in an alternative separation. Sulphate mother-liquors rich in *meso*-diamine were rendered alkaline with ammonia, extracted with benzene, the base converted into sulphate, and this salt crystallised repeatedly from alcohol until it melted at 206° (Found: S, 9·5. $C_{16}H_{20}N_2,H_2SO_4$ requires S, 9·5%).

Azo-dyes from Diphenyl-βγ-*diamino*-n-*butane*.

dl-*Di*-4′-*sulphobenzenedis*-4-*azodiphenyl*-βγ-*diamino*-n-*butane* (III).—*dl*-Diphenyl-βγ-diamino-*n*-butane (3·5 g.; 1 mol.), dissolved in 3·5 c.c. of concentrated hydrochloric acid and 10 c.c. of water, was added gradually to a solution of benzene-*p*-diazoniumsulphonate prepared from 5 g. of sulphanilic acid (2 mols.); a dark red disazo-dye separated (8 g. or 91%). This product dissolved readily in alcohol or glacial acetic acid, but was less soluble in acetone and insoluble in other organic solvents or water; it was dissolved in the minimum amount of dilute ammonia and reprecipitated by acid as a dark red, amorphous powder with bronzy reflex. The

dye developed intensely red colorations with concentrated mineral acids, had no definite melting point, but decomposed at 194°.

The *potassium* salt, obtained as a viscid solid by concentrating the solution of the dye in aqueous potassium carbonate, crystallised in an anhydrous form from dilute alcohol in small, orange needles (Found: K, 11·5; S, 9·3; azo-N_2 by titanous chloride, 8·1. $C_{28}H_{26}O_6N_6S_2K_2$ requires K, 11·4; S, 9·35; azo-N_2, 8·2%).

Dyeing Properties of the Racemoid Colouring Matter.—In the presence of sodium sulphate and sulphuric acid the dye liberated from its potassium salt in dilute solution dyed wool in deep orange shades, the colour being stripped by ammonia or strong soap solution.

Silk was dyed in boiled-off liquor and developed in a 1% sulphuric acid bath, giving golden-yellow shades. The partially exhausted solutions were examined in the polarimeter, a 12-volt, 24-watt Siemens lamp being used as a source of light (the wave-length being 6708 Å.). No activity was developed in the dye-bath whether the solvent employed was water, dilute alcohol, or 30% acetic acid, the strength of the dye-bath being approximately 0·75%.

In their successful attempt to show selective action of wool on a racemoid dye Porter and Ihrig (*loc. cit.*) used glacial acetic acid as solvent. The dye was employed in 1% solution, the quantity was 40% of the weight of wool, and the dyeing was carried out at 20° for 48 hours. A similar experiment was made taking 1 g. of dye in 75 c.c. of 30% acetic acid; 2·5 g. of wool were dyed at 20° for 24 hours. No activity was noticed at first, but after 72 hours a slight lævorotation was observed. Experiments with wool and silk using alcohol and dilute sulphuric acid as solvent for the dye showed no activity. These experiments on the racemoid dye did not furnish decisive evidence of preferential dyeing with either enantiomorph.

Resolution of dl-4′-*Sulphobenzenedis*-4-*azodiphenyl*-βγ-*diamino*-n-*butane.—Brucine salt.* Brucine acetate (2·65 g. or 2 mols.) in 20 c.c. of water was added to 2 g. of the potassium salt of the dye in 50 c.c. of water. The dibrucine salt of the dye separated as a brownish-yellow precipitate (decomposition point 189°); it was moderately soluble in chloroform, but insoluble in other organic media or water. From chloroform alone and from this solvent mixed with light petroleum the brucine salt separated in shellac-like or viscid forms, but not in a crystalline condition (Found: azo-N_2 by titanous chloride, 4·0. $C_{28}H_{28}O_6N_6S_2,2C_{23}H_{26}O_4N_2$ requires azo-N_2, 4·0%). The analysis showed that the substance was a dibrucine salt (2 mols. B + 1 mol. azo-compound).

The *strychnine* salt was prepared from strychnine hydrochloride and the potassium azo-dye salt as in the preceding preparation.

The bright yellow precipitate was readily soluble in chloroform, less soluble in alcohol or acetone, and insoluble in other organic media or water. When a dilute solution in absolute alcohol was allowed to evaporate very slowly, the strychnine salt separated in small needles, decomp. 179° (Found : azo-N_2, 4·4; total N, 11·1, 11·2. $C_{28}H_{28}O_6N_6S_2,2C_{21}H_{22}O_2N_2$ requires azo-N_2, 4·4; total N, 11·0%).

The strychnine salt was crystallised repeatedly from alcohol, the least soluble portions were examined polarimetrically, and crystallisation was continued until the rotation was constant: $[\alpha]^{17°}_{5563} = -308·3°$ for a 0·96% alcoholic solution ($l = 0·5$).

The salt having this specific rotation was warmed gently with aqueous potassium carbonate. The filtrate from strychnine was extracted repeatedly with chloroform to remove any of this base remaining in solution. The aqueous solution was allowed to evaporate, when the active potassium salt of the resolved dye separated slowly. A 0·99% solution gave $\alpha^{17°}_{6563} - 1·02°$ ($l = 0·5$) or $[\alpha]^{17°} = -206°$, $[M]^{17°} = -1409°$. The *l*-potassium salt, like its *dl*-isomeride, was anhydrous (Found : total N, 12·5; azo-N_2, 8·15, 8·2; K, 11·5. $C_{28}H_{26}O_6N_6S_2K_2$ requires total N, 12·3; azo-N_2, 8·1; K, 11·4%).

The mother-liquors from the lævorotatory strychnine salt were examined for the *d*-salt, but the more soluble fractions were viscid and on decomposition with potassium carbonate did not yield any dextrorotatory potassium salt.

Cinchonidine salts. The two stereoisomeric potassium salts were ultimately obtained through the cinchonidine salts. A solution of 2 g. (2 mols.) of cinchonidine hydrochloride in 20 c.c. of water was added to 2 g. of *dl*-potassium salt in 50 c.c. of water, when a yellow precipitate of the cinchonidine salt was obtained almost quantitatively (Found : total N, 11·9, 11·8; azo-N_2, 4·6, 4·7. $C_{28}H_{28}O_6N_6S_2,2C_{19}H_{22}ON_2$ requires total N, 11·7; azo-N_2, 4·7%).

The cinchonidine salt decomposing at 176° was moderately soluble in chloroform or alcohol, slightly soluble in benzene, but insoluble in other organic solvents and in water. By slow evaporation of a dilute alcoholic solution the cinchonidine salt was obtained in small needles and this crystallisation was repeated until the rotation was constant. A 0·97% solution gave $\alpha^{18°}_{6563} - 1·32°$ ($l = 0·5$) or $[\alpha]^{18°}_{5563} = -272°$.

This less soluble salt was decomposed by warming with aqueous potassium carbonate. The filtrate from cinchonidine was extracted repeatedly with chloroform to remove any traces of the alkaloid remaining in solution. The lævorotatory *potassium* salt (0·99% solution) gave $\alpha - 0·87°$, $[\alpha]^{16·3°} = -176·1°$, $[M]^{16·3°} = -1204°$

(Found: total N, 12·4; azo-N_2, 8·1, 8·15. $C_{28}H_{26}O_6N_6S_2K_2$ requires total N, 12·3; azo-N_2, 8·2%).

The dextrorotatory potassium salt. The cinchonidine salt of the dextrorotatory acid was isolated by concentrating the mother-liquor from the foregoing less soluble cinchonidine salt. The more soluble portions were crystallised repeatedly from alcohol until the rotation was constant; a 0·99% solution gave $\alpha - 0·29°$; $[\alpha]^{17°} = - 58·4°$.

The cinchonidine was then set free by aqueous potassium carbonate and the last traces were removed by chloroform. The aqueous solution slowly deposited the dextrorotatory potassium salt; a 0·977% solution gave $\alpha + 0·82°$; $[\alpha]^{18°} = + 167·8°$, $[M]^{18°} = + 1147·8°$ (Found: K, 11·5; azo-N_2, 8·1. $C_{28}H_{26}O_6N_6S_2K_2$ requires K, 11·4; azo-N_2, 8·2%).

The lævo- and dextro-rotatory potassium salts as obtained by the resolution with cinchonidine are in agreement with regard to optical activity, whereas the lævo-salt obtained through the strychnine resolution is more active. These differences, although not entirely explained, are not due to contamination with alkaloids, for these were recovered quantitatively. The resolution was probably more complete in one case than the other.

In the course of the attempts to isolate the dextro-form of the dye the following alkaloidal salts were prepared: *Morphine* salt, brownish-yellow precipitate insoluble in water or organic media, charring at 184°; *codeine* salt, a viscid, brownish-yellow mass more soluble in water than the other alkaloidal salts; *cinchonine* salt, brownish-yellow, amorphous powder fairly soluble in alcohol or chloroform, less so in acetone, but practically insoluble in other media or water; decomposed at 192°.

meso-*Di*-4′-*sulphobenzene*-4-*disazodiphenyl*-βγ-*diamino*-n-*butane*.—This substance was prepared in order to complete the series *dl*, *d*, *l*, and *meso* of the stereoisomeric azo-acids by adding 0·9 g. (1 mol.) of *meso*-diphenyl-βγ-diamino-*n*-butane dissolved in 1 c.c. of concentrated hydrochloric acid and 5 c.c. of water to a solution of benzene-*p*-diazoniumsulphonate from 1·3 g. (2 mols.) of sulphanilic acid. The dark red *meso*-azo-dye was precipitated (yield 87%). It was slightly soluble in alcohol or glacial acetic acid and almost insoluble in other organic media or water. It was purified through the potassium salt (Found: K, 11·5; S, 9·3. $C_{28}H_{26}O_6N_6S_2K_2$ requires K, 11·4; S, 9·35%).

This *meso*-azo-acid and its salts are more stable and less soluble than the corresponding externally compensated compounds. The *codeine* salt of the *meso*-acid is very insoluble, thus differing from the codeine salt of the *dl*-acid.

Rates of Absorption by Wool of the Stereoisomeric Azo-dyes (*dl*-, *l*-, and *meso*-forms).—The experiments with the four stereoisomerides were arranged to run concurrently, the dyeings being carried out in a thermostat at 20°. At intervals of 3, 24, 48, 72, and 96 hours, 5 c.c. of solution were removed and the amount of azo-dye was estimated by titration with dilute titanous chloride. The solutions of the dyes were made in 50% acetic acid.

I. Racemoid form : 2·4642 g. of wool in 100 c.c. of solution with 0·4576 g. of dye.
II. *Dextro*-form : 2·4886 g. of wool in 101 c.c. of solution with 0·4621 g. of dye.
III. *Lævo*-form : 2·4691 g. of wool in 100·2 c.c. of solution with 0·4555 g. of dye.
IV. *Meso*-form : 2·5007 g. of wool in 101·5 c.c. of solution with 0·4644 g. of dye.

Time (hours).	Amount (g.) in 5 c.c. of solution. I.	II.	III.	IV.
0	0·02288	0·02288	0·02288	0·02288
3	0·02276	0·02265	0·02278	0·02277
24	0·02153	0·02144	0·02164	0·02205
48	0·02024	0·02016	0·02033	0·02138
72	0·01923	0·01909	0·01933	0·02081
96	0·01887	0·01866	0·01896	0·02047

These tabulated data show that the dextrorotatory isomeride is absorbed by wool at a consistently though only slightly faster rate than the racemoid form and that the lævorotatory form is absorbed less rapidly than either the *dl*- or *d*-form, which result is in agreement with the polarimetric indications obtained (p. 1736) in the experiments on the selective action of wool on the racemoid azo-dye. A slight development of lævorotatory activity was detected in the dye-bath.

The *meso*-form is absorbed less readily than any of its three isomerides.

The differences in the rates of absorption of the *d*- and *l*-forms show that selective absorption from a racemoid mixture is quite feasible, but in the case of the sulphonated dyes examined in the preceding experiments the differences were not sufficiently large to admit of direct measurements of optical activity. Hence further experiments were made with less acidic carboxylated azo-dyes.

dl-trans-2′-*Carboxybenzene*-4-*azodiphenyl*-βγ-*diamino*-n-*butane* (VI).—An ice-cold solution of benzene-1-diazonium-2-carboxylate, prepared from 5 g. of anthranilic acid (1 mol.), 3·5 c.c. of concentrated hydrochloric acid and 2·5 g. of sodium nitrite in 60 c.c. of water, was added to 4·25 g. (1 mol.) of *dl*-diphenyl-βγ-diamino-*n*-butane dissolved in 15 c.c. of water containing 2 c.c. of glacial acetic acid and 2·5 g. of sodium acetate, when a dark red dye was precipitated.

After 3 hours the coupling was completed by warming on the water-bath. The dye was then collected and washed with ether to remove salicylic acid formed by hydrolysis of the diazonium salt (yield 78%).

Crystallised from 50% acetic acid, the red azo-dye separated in small, dark red needles, decomp. 113°. It was readily soluble in glacial acetic acid, less soluble in methyl and ethyl alcohols, and sparingly soluble in water. It exhibited amphoteric properties, being soluble either in mineral acids or in aqueous ammonia. The atter solution was used in purifying the dye, for on concentration the ammonium salt crystallised. The free acid was subsequently crystallised from glacial acetic acid (Found: total N, 14·6; azo-N_2, 7·1, 7·15. $C_{23}H_{24}O_2N_4$ requires total N, 14·4; azo-N_2, 7·2%). These analyses show that the compound is a monoazo-dye, only one diazo-group being coupled with the diamine.

The monoazo-colouring matter dyed wool in brownish-red shades and silk in dark salmon shades. Experiments were made with this racemoid monoazo-dye with varying conditions as to solvent, time of contact, and concentration of solution as with the racemoid sulphonated disazo-dye, but in no case was there any indication of optical activity.

Resolution of the Racemoid Carboxylated Dye.—The *strychnine* salt was obtained as a red precipitate on adding 1·8 g. of strychnine hydrochloride (1 mol.) in 25 c.c. of water to 2 g. (1 mol.) of the ammonium salt of *dl-trans*-2′-carboxybenzene-4-azodiphenyl-βγ-diamino-*n*-butane dissolved in 50 c.c. of water. This salt dissolved readily in alcohol or chloroform, more sparingly in acetone, but was practically insoluble in other organic solvents and in water. From its alcoholic solution the salt separated on slow evaporation in small needles, decomp. 121° (Found: total N, 11·8; azo-N_2, 3·8. $C_{23}H_{24}O_2N_4$,$C_{21}H_{22}O_2N_2$ requires total N, 11·6; azo-N_2, 3·9%).

Resolution was effected by repeated crystallisation in absolute alcohol until a constant value was obtained for the optical activity; 1% alcoholic solutions were employed with light of wave-length 6708 Å. A 1·02% solution gave α — 0·41° (l = 0·5); $[\alpha]^{19°}$ = — 80·5°. This strychnine salt was decomposed by warming gently with the calculated amount of ammonium carbonate in aqueous solution. The strychnine was precipitated, and the solution extracted repeatedly with chloroform to remove traces of the alkaloid. The filtrate was concentrated in a vacuum at the ordinary temperature until the ammonium salt crystallised. Approximately 1% aqueous solutions of this ammonium salt were examined polarimetrically. A 1·10% solution gave α — 0·24°; $[\alpha]^{16°}$ = — 43·7°,

hence $[M]^{16°} = -169{\cdot}6°$ (Found: azo-N_2, 6·8. $C_{23}H_{27}O_2N_5$ equires azo-N_2, 6·9%).

Attempts were now made to isolate the *dextro*-form of the azo-ompound from the more soluble mother-liquors from the *l*-strych-ine salt, but it was found impossible to obtain an even slightly extrorotatory ammonium salt. Other alkaloids such as brucine, iorphine, codeine, cinchonine and cinchonidine did not assist in ringing about this resolution.

dl-cis-2′-*Carboxybenzene*-4-*azodiphenyl*-βγ-*diamino*-n-*butane* (V).—nthranilic acid was diazotised and coupled with *meso*-diphenyl-γ-diamino-*n*-butane, when, owing to the circumstance that the iazonium carboxylate coupled with the diamine in molecular roportions, the resulting monoazo-derivative was no longer a *neso*-compound having internal compensation, but was capable f resolution.

The red dye crystallised from 50% acetic acid in small, red eedles, decomp. 116°; its solubility and dyeing properties are imilar to those of the corresponding *dl-trans*-compound (Found: zo-N_2, 7·15. $C_{23}H_{24}O_2N_4$ requires azo-N_2, 7·2%).

Rates of Absorption by Wool of the Stereoisomeric Carboxylated lzo-dyes.—The experiments were carried out precisely as de-cribed on pp. 1732, 1739, excepting that the solutions were made p with 30% acetic acid.

I. *dl-trans*-Form: 5·0116 g. of wool in 200 c.c. of solution with 1·2768 g. of dye.
II. *l-trans*-Form: 5·1334 g. of wool in 205 c.c. of solution with 1·3074 g. of dye.
III. *dl-cis*-Form: 5·0521 g. of wool in 201·6 c.c. of solution with 1·2870 g. of dye.

Time (hours).	Amount (g.) in 5 c.c. of solution. I.	II.	III.
0	0·03192	0·03192	0·03192
3	0·03148	0·03151	0·03150
24	0·02802	0·02929	0·02849
46	0·02503	0·02685	0·02546
72	0·02359	0·02454	0·02377
98	0·02282	0·02337	0·02298
120	0·02253	0·02283	0·02263

The foregoing data showed that the *cis*- and *trans-dl*-forms were bsorbed at practically the same rate and that the active lævo-rm was absorbed less rapidly than the corresponding racemoid rm, the difference in these rates of absorption being rather greater an in the case of the sulphonated azo-dyes.

Note on the Sulphonation of dl-*Diphenyl*-βγ-*diamino*-n-*butane.*

Treatment of this diamine with oleum (up to 20% SO_3) led to ydrolytic decomposition, so that the sulphonated product was

sulphanilic acid. Chlorosulphonic acid also gave rise to com plicated reactions and the formation of complex sulphonate sulphones. By neither treatment was a simple sulphonated pr duct of the base obtained, so that the attempt to resolve th *dl*-diamine through its sulphonic acid was abandoned.

The authors desire to express their thanks to the Researc Committee of the University of Birmingham and to the Advisor Council of the Department of Scientific and Industrial Researc for grants which have helped to defray the expense of th investigation.

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CCXXXI.—*Theories of Polar and Non-polar Fre Affinities. A Practical and Theoretical Reply t some Recent Criticisms and Comparisons.*

By GEORGE NORMAN BURKHARDT and ARTHUR LAPWORTH.

IN a paper by C. K. Ingold (J., 1924, **125**, 93) the following sentence occur :

" The establishment of this formula provides an interesting tes of the hypothesis by means of which so many obscure points i chemistry are nowadays ' explained.' In nitrosobenzene oxygen i the ' key-atom '(Lapworth, T., 1922, **121**, 416), and the compoun may be represented as $C_6H_5—\overset{+}{N}=\overset{-}{O}$."

The sentences are misleading in several ways. As only on reference to the literature is given, it is necessary to point out (1 that Lapworth had never discussed the case of nitrosobenzene an (2) that the phrasing of the second sentence shows that Lapworth' conception of key-atoms is misunderstood. Ingold here, as else where (this vol., p. 514), confuses the conception with the earlie one of Flürscheim. Both theories attribute to bivalent oxyge for example, a special capacity to affect the properties of the rest o the molecule; Flürscheim's theory, however, postulates a fixe configuration for each compound, and Lapworth's (like that o Kermack and Robinson) does not.

The assumption that all " polarity theories " conform to the sam regulations as Flürscheim's is the origin of a number of misdirecte criticisms. When the inaptness of this line of attack is realised the critics substitute the objection that those theories are so flexibl as to have no prophetic power in potential test cases (compare C. K

nd E. H. Ingold, this vol., p. 871). This peculiarity merely shows, owever, that the cases thought of are not test cases at all. Some eal test cases are mentioned later in the present paper.

The doctrine that theories such as those of Thiele and Flürscheim re not so flexible in their application as polarity theories is widely reached, and in view of its reappearance in the paper last mentioned it becomes necessary to prove that it is a fallacious one, in airness to the theories disparaged.

The theories of fixed non-polar free affinities * certainly give nequivocal and correct correspondence with fact, but only within ertain limited ranges. Outside those ranges they show on the same asis an unequivocal disagreement with fact. Thiele's form explains " the ordinary additive reactions of carbonyl correctly, ut on the same principle foretells *o*-*p*-substitution in benzaldehyde. 'lürscheim's form explains *m*-substitution in benzaldehyde, but ignally fails to explain the additive properties of carbonyl compounds. Flürscheim explains meta-substitution in benzaldeyde by assuming that the agent first attacks the meta-carbon tom; but he explains cyanohydrin formation by assuming that he agent first attacks the oxygen atom (*Chem. and Ind.*, 1925, **44**, 72).

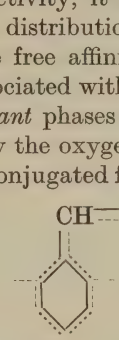
Another excellent example of this is found in the explanation ffered for the addition of potassium carbazole to nitrobenzene, here the potassium attaches itself to an oxygen atom and the arbazole residue to the para-carbon atom (*ibid.*, 173): or, looking t it in a slightly different way, Flürscheim here throws over his own ormula and adopts Thiele's, its exact opposite. In these systems, herefore, there are nearly always two such possibilities and to uote Flürscheim's words in a similar connexion, " whichever way he experiment goes, one of these alternatives is bound to fit and hichever fits is adopted from case to case " (*ibid.*, 1925, **44**, 84). uch a process of reasoning is, of course, appropriate for the theory hich deduces configuration from observed facts, but is not dmissible for one which claims to predict facts from *a priori* onsiderations.

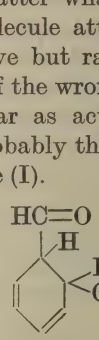
The claim that no arbitrary factor enters into the so-called

* The description of an hypothesis or a theory such as that of Flürscheim s one of " alternating affinity demand " cannot be used to distinguish it om theories of Kermack and Robinson or Lapworth which also postulate ternating affinity demands. It is necessary, therefore, to protest ematically against the terminology adopted in the above paper of Ingold nd Ingold (*loc. cit.*, p. 870) as likely to spread the perplexity to which one these authors has frankly confessed (this vol., p. 514, footnote). No uestion of priority can be admitted as sufficient reason for an implied istinction which does not exist.

predictions of the non-polar theories is therefore one which cann be taken seriously. No similar claim has ever been made by a responsible exponent of the polarity theories which Ingold discuss Polarity theories are acknowledged to be in a state of evolution a at present function properly as aids to interpretation, not substitutes for intellectual effort.

Polarity considerations solve some of the difficulties inseparab from the theories of Thiele and Flürscheim and in a very simp and logical way, because, with a polar agent which has consiste polar selectivity, it is evident that no matter what may be t dominant distribution of affinity in a molecule attacked by th agent, the free affinity will not be effective but rather inhibiti if it is associated with an electrical charge of the wrong sign. Thu the *dominant* phases of benzaldehyde, so far as activation of t nucleus by the oxygen is concerned, are probably those correspon ing with conjugated forms of the Thiele type (I).

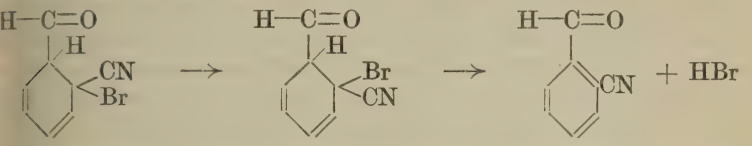
(I.) 

 (II.)

This corresponds with Robinson's "crotonoid" forms (*Che and Ind.*, 1925, **44**, 456) and the polarities of the excess free affiniti in the *o*- and *p*-carbon atoms are mainly positive, as the relati of these positions to the predominating key-atom in the conjugat system shows. The ordinary types of substitution in benzene, su as nitration, sulphonation, bromination, and diazonium couplin require a negative free affinity at the carbon atom at which subst tution of hydrogen takes place. Consequently with benzaldehyd phases of the above type are almost or quite inert towards su agents, substitution is very slow and perhaps takes place on in other phases of rare occurrence in the reacting system.

The circumstance that benzaldehyde is not known to pick u negative ions like cyanidion at the *o*- and *p*-positions in the nucleu although it does so readily at the carbonyl carbon atom, is not the least incompatible with the above view. The addition reactio of αβ-unsaturated carbonyl compounds with electrolytes a reversible, and in view of this, as well as the known tendency dihydro-derivatives to revert to benzenoid types, it is practical certain that the expected addition product (II) is a compound whi would not exist in any considerable proportion in equilibrium wi benzaldehyde and hydrogen cyanide. By introducing any oth conditions which would permit the initial addition compound wi

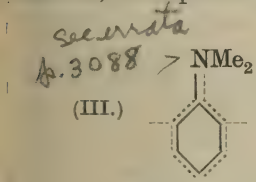
hydrogen cyanide to revert to an aromatic type in a different way, vidence might be obtained of the formation of that compound; such a condition would possibly be provided in *o*-bromobenzaldehyde, as the addition product here could react as follows if *cis-trans* change occurs before reversion :



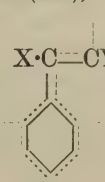
This case would be exactly comparable with the ready replacement of halogen by hydroxyl in the *o*- and *p*-chloronitrobenzenes, which is claimed, not as a prediction from polar theories, but only as part of the evidence in favour of them.

Not less important and obviously very intimately connected with the known reversibility of the negative ion additions to αβ-unsaturated compounds, is the circumstance that tervalent carbon appears to tolerate a positive charge much more readily than it does a negative charge, and $\overset{\oplus}{C}H_3$ has frequently been detected by Sir J. J. Thomson in vacuum-tubes but $\overset{\ominus}{C}H_3$ never. Other things being equal, therefore, positive free valencies on aromatic carbon and on ethylenic carbon appear inert in comparison with negative free valencies.

In the case of phenol ethers, dialkylanilines and many others, the dominant conjugated forms or phases also have their excess free affinities in the *o*- and *p*-positions. Their structures, apart from polarities, correspond with Flürscheim's idea (III),



(III.)



(IV.)

but here the excess free affinities on the carbon atoms in the nucleus are negative; hence ordinary substitution compared with substitution in benzene is very rapid, and certain active positive ions (*e.g.*, diazonium ions) can attach themselves to the active *o*- and *p*-carbon atoms, but never negative ions. Form (III) also corresponds with Robinson's "crotenoid" forms (*loc. cit.*). If the two exterior atoms in (I) are singly bound to each other, conjugation can take place only to that very limited extent which corresponds with the

relatively feeble transmission of alternate polarities through tw single bonds.

The third type of conjugation, present in styrene, leads, in th ring, to excess valencies in the *o*-*p*-positions (IV); this obvious facilitates substitution in the nucleus when the excess free affiniti in the nucleus are the *negative* ends of the conjugated systems an *o*-*p*-substitution therefore results. In phases where these affiniti represent the *positive* ends, substitution takes place at the carbo atom once removed from the nucleus, where the negative free affinit is now found, so that, in competition with a group like carbon (and *a fortiori* with a group of the type $-\dot{\underset{\cdot\cdot}{C}}-\dot{O}R$), which, by conju gation, normally produces only phases with inhibited reactivit towards ordinary substituting agents, the group CX=CYH wi normally appear by far the more effective. α-Methoxystyren provides an instance of such competition within the same side-group

The present position is therefore this. Supporters of pola theories accept the general ideas of conjugation and of alternat affinity demand, but do not admit that there is any real distinctio between these two conceptions. They hold, however, that thes ideas have often been wrongly applied, and have little real predi ative power until polar considerations are introduced. It is equall true that the principle of induced alternate polarities is likely to b barren until considered simultaneously with conjugation and othe factors; *but this was pointed out in Lapworth's original paper* (*Mem Manchester Phil. Soc.*, 1920, **64**, ii, 10, last par.) which, it woul seem, is rarely consulted.

In the original paper (*loc. cit.*, p. 6), where the general idea " key-atoms " was broadly indicated, the molecule of formic aci was selected to illustrate that idea. It was explained that i considering different properties of formic acid sometimes oxygen an sometimes hydrogen was considered to be the " key-atom." Th " key-atom " in fact, as imagined by Lapworth, is not always th same in the same compound, but is any atom to the alternat inductive effect of which certain properties of the molecule are du On this conception, the effects of two " key-atoms " may be super imposed—perhaps are always so to some extent—or may so operat that each in turn may determine the properties in different phase of the same molecule (*loc. cit.*). The expression " the key-atom should be applied only to the atom which is considered respon sible for a certain effect and not merely to the one which produce the most striking effects or even to one which has an effect on ever property. A suggestion often heard that the introduction of th term " key-atom " merely corresponds with a christening

Flürscheim's fixed and also non-polarising atom is therefore but a uarter-truth.

It is possible now to return with advantage to Ingold's statement, iven at the beginning of the present paper.

As Ingold, with Weaver, has already pointed out (J., 1924, **125**, 458), there are many close analogies between the addition reactions f the nitroso-group and those of carbonyl. In fact, it may be said hat in such cases no evidence has ever been obtained that requires he introduction of the scheme $C_6H_5-\overset{-}{N}=\overset{+}{O}$. In reactions where the xygen is not directly involved, Ingold's remarks could not in any ase apply.

Ingold, however, in the paper first quoted, claimed to have roved that when nitrosobenzene combines with (*a*) methylene-nilines, compounds with four-membered rings are formed, the irection of addition being exactly the opposite of what the usual olarity ideas demand. In the later paper with Weaver (*loc. cit.*) e made similar claims for the reactions of nitrosobenzene with) hydrocarbons like styrene and diphenylethylene, (*c*) with ıethylenemalonic ester respectively.

Whilst his later experiments on nuclear substitution in nitroso-enzene and α-methoxystyrene (this vol., pp. 513, 870) introduce o new theoretical difficulties (having given exactly those results hich were to be expected), his interpretations of those three types f reaction mentioned in the preceding paragraph are difficult to :oncile with the usual polar additive properties of the compounds. s these interpretations were apparently based on very slender xperimental evidence, it was decided to re-examine these three ghly interesting cases. The fallacy in case (*c*) has already en detected and may now be dealt with.

Ingold and Weaver (J., 1924, **125**, 1459) found that nitrosobenzene id ethyl methylenemalonate combined to give a crystalline com-ound. They describe some of the properties of the compound in ie following terms: "it gives no colour with ferric chloride, no pper salt, and is oxidised by alkaline permanganate only with fficulty." The constitution ascribed to it was (V) and the forma-on of this compound was included among the cases in which "the rection of the addition is contrary to the indications of the polar eory." It was maintained that the polarity theory requires the rmation of (VI).

(V.) $\begin{matrix} CH_2—C(CO_2Et)_2 \\ | \quad\quad | \\ C_6H_5\cdot N——O \end{matrix}$ $\qquad$ $\begin{matrix} CH_2—C(CO_2Et)_2 \\ | \quad\quad | \\ O——N\cdot C_6H_5 \end{matrix}$ (VI.)

he present authors first prepared the product by the same method, ut observed that, although no crystalline copper derivatives could

be isolated, with their specimens a strong maroon coloration wa always produced when copper acetate was added to an alcohol solution of the compound.

The compound was a very sensitive one and was rapidly oxidise even in the cold by alcoholic ferric chloride, the odour of nitroso benzene becoming very perceptible in a minute or two; nitroso benzene was easily isolated by diluting the resulting solution wit water and extracting with ether. Although apparently stable t aqueous permanganate, doubtless owing to its sparing solubility i water, the compound was rapidly oxidised by permanganate in col acetone. It was evident that the properties of the compound wer not consistent with the ring formula previously ascribed to it. A Ingold and Weaver had furnished no direct evidence that th oxygen atom of the nitrosobenzene had taken any part in the act union, the following experiment was tried :

Ethyl hydroxymethylenemalonate (3 g.) is dissolved in 60% col methyl alcohol (10 c.c.), β-phenylhydroxylamine (2 g.) is adde when the solid dissolves at once. After 1 or 2 minutes, water added in sufficient quantity to cause a turbidity. (In the firs experiment no crystals were deposited until a trace of the solid prepared by Ingold and Weaver's method, was introduced, when th whole at once set to a sludge of needles which increased in quantit on further addition of water.) The product (3—3·5 g.) is filtere off, dried, and crystallised from dilute methyl alcohol. The com pound so made forms slender needles, m. p. 98—99°, and is identic in all respects (including the intensity and duration of the coloratio given in alcoholic solution with copper acetate) with the compoun previously described as " ethyl 2-phenyldimethylene-1 : 2-oxaimin 4 : 4-dicarboxylate " (Found : C, 60·0; H, 6·4. Calc., C, 60· H, 6·1%).

The compound, then, is one of the possible dynamic isomerid of the *N*-phenyloxime of the ester-aldehyde $O{:}CH{\cdot}CH(CO_2Et)$ of which ethyl hydroxymethylenemalonate, $HO{\cdot}CH{:}C(CO_2Et)$ is the enolic form. The *N*-phenyloxime of this aldehyde-est would be $O{:}N(C_6H_5){:}CH{\cdot}CH(CO_2Et)_2$ or, in modernised form $\overset{\ominus}{O}{\cdot}\overset{\oplus}{N}(C_6H_5){:}CH{\cdot}CH(CO_2Et)_2$. The dynamic isomeride of this corr sponding with ethyl hydroxymethylenemalonate is of cours $HO{\cdot}N(C_6H_5){\cdot}CH{:}C(CO_2Et)_2$ and it is scarcely possible to state wit certainty to which of these formulæ the solid itself correspond The behaviour of the compound in alcoholic solution with copp acetate, however, recalls that of the monoalkylated acetoacetic ester which also give evidence of the formation of dissociable copp derivatives in similar circumstances. It is as likely as not, therefor

non-hydroxylic form, or *dicarbethoxymethyl*-N-*phenylnitrone*, esponds with the solid and with the one which preponderates olution. Reference may be made to the work of Alessandri zzetta, 1924, **54**, 426) and others on the formation of *N*-phenyl-ones from nitrosobenzene and ethylenic compounds.

n the polarity theory, the first step in the process of union of ethylenic portion of ethyl methylenemalonate with nitroso-zene must be the union of the tervalent nitrogen of the nitroso-up with the β-carbon atom of the ester. This carbon atom has ery marked and quite consistent latent or real positive polar racter and the first addition process corresponds with ammonium formation :

$$\begin{matrix} CH_2{=}C(CO_2Et)_2 \\ O{=}N{\cdot}C_6H_5 \end{matrix} \longrightarrow \begin{matrix} CH_2{-}[C(CO_2\overset{\ominus}{E}t)_2] \\ O{=}\underset{\oplus}{N}{\cdot}C_6H_5 \end{matrix} \quad \text{(VII.)}$$

his initial product (VII) is a bipolar ion (to adopt Lowry's venient nomenclature), or internal ammonium salt; the signs wn in circles are electrical charges, the positive charge being ciated with the ammonium residue; the negative charge is e associated with a residue comparable in every way with the atively charged organic residue of ethyl *sodio*malonate.

tabilisation and internal neutralisation of this initial product sequently occur by " migration " of proton, or exchange of ton with the surrounding molecules in one or more of several sible ways.

he above conclusions are wholly consistent with our knowledge nitrones, with Lapworth's explanation of the polar additive tions of αβ-unsaturated carbonyl compounds (J., 1904, **85**, 1212), with Robinson's interpretation of the polar reactions of nitroso-zene (*Chem. and Ind.*, 1925, **44**, 456). The formation of addition ducts of ammonia, and primary and secondary amines, with nsaturated carbonyl compounds, nitriles, etc., can evidently explained on very similar lines, stabilisation and internal tralisation of the bipolar ions in such cases also taking place by roton migration or interchange, but in a slightly different mode.

will be instructive for those who have not previously followed various non-polar theories to their logical conclusions to observe the β-carbon atom of ethyl methylenemalonate is the one which s part in the actual union of the molecule of this compound with osobenzene. Now Flürscheim's theory of " orientation " in aromatic series postulates that the meta-orienting effect of group of compounds which includes carbethoxyl depends on the mption that these groups make a smaller affinity demand than

hydrogen, and this results in the development of an excess of f affinity at the meta-carbon atom in the ring, so that the ag attacks the meta-carbon atom preferentially. Applying t argument to ethyl methylenemalonate, it is obvious that repla ment of two hydrogens unsymmetrically in the symmetri ethylene (VIII) by carbethoxyl must lead to the affinity dist bution represented by (IX): or, expressed in words, the α-carb

(VIII.) $CH_2=CH_2$ $\qquad$ $CH_2=C<^{CO_2Et}_{CO_2Et}$ (IX.)

atom must have now a greater amount of unbound affinity than t β-carbon atom and therefore the α-carbon atom should be the c at which union with nitrosobenzene takes place: a predicti which fails.

It is not a little remarkable, therefore, that a reaction origina considered to be evidence against the polarity theory provides, wh more closely examined, the most elegant known demonstrati of the incorrectness of the Werner-Flürscheim theory. Hithe the most complete disproof would have involved a lengthy mat matical demonstration that it is impossible to construct mass-l equations which shall be capable of explaining the kinetics of t addition of the elements of hydrogen cyanide to cyanoacrylic aci where the nitrile group corresponds with the carbethoxyl grou (which correspond closely with ethyl methylenemalonate in stru ture), on any other hypothesis than that the first step in the additi process involves the union of the β-carbon atom with cyanidi (W. J. Jones, J., 1914, **105**, 1547, 1560. Compare also Lapwor J., 1903, **83**, 995; 1904, **85**, 1208).

All these facts, together with what is known of the conditions formation and decomposition of the cyanohydrins of simple al hydes and ketones, show that the revival of the Werner-Flürsche hypothesis can only have the effect of diverting attention fr important issues which have not yet been decided.

Lapworth stated in 1920 that bivalent oxygen is usually m effective than tervalent nitrogen, but the statement had refere to statistical aspects only. Enough is known to show that t dominance of either atom depends on many varying circumstan and the question whether these more frequently favour biva oxygen than tervalent nitrogen is not worth debating.

Note added July 12th, 1925.—Compare, on this point, *Chem. & Ind.*, 1925, **44**, 713.

THE UNIVERSITY, MANCHESTER. [*Received, May 16th*, 1925.]

CCXXXII.—*The Estimation of Arsenic in Organic Compounds.*

By George Newbery.

The most accurate and trustworthy method for the estimation of arsenic in organic arsenical compounds is undoubtedly that in which the arsenic is oxidised by the Carius method to arsenic acid and subsequently weighed as magnesium pyroarsenate. The methods in general use which have been devised in the endeavour to combine the accuracy of this procedure with greater simplicity and rapidity are those of Lehmann (*Apoth. Ztg.*, 1912, **27**, 545) and the modifications suggested by Fargher (J., 1919, **115**, 992) and Myers and Dumez (*U.S. Public Health Rep.*, 1918, **33**, 1003), that of Ewins (J., 1916, **109**, 1355) and of Robertson (*J. Amer. Chem. Soc.*, 1921, **43**, 182). The first of these involves a volumetric determination of doubtful accuracy (compare criticism by Gooch and Morris, *Amer. J. Sci.*, 1900, **10**, 151 and many others); the other two are somewhat tedious in the procedure proposed for the decomposition of the arsenical, and the high temperatures involved render possible some slight loss of arsenic by volatilisation (Myers and Dumez, *loc. cit.*).

The use of ammonium persulphate (in conjunction with nitric acid) for this decomposition has been suggested by Rogers (*Can. Chem. J.*, 1920, **3**, 398) and that of persulphate alone has long been employed in these laboratories. The following process involves this method of oxidation. With the majority of substances to which the method has been applied a determination in duplicate can be completed in the course of an hour: with a few, the boiling down with persulphate has to be prolonged and even repeated with a larger quantity, in order that a colourless solution may be obtained. The decomposition in the case of insoluble substances of acid character is facilitated by solution in caustic alkali before the addition of persulphate, the acid being thus thrown out in a finely divided condition. The details are as follows:—

A mixture of the substance (0·2 g.), 20 c.c. of water, and 4—5 g. of ammonium persulphate is heated to brisk ebullition in a 300 c.c. Erlenmeyer flask, provided with a device to prevent loss by spraying. When the mixture is quite colourless (usually less than 10 minutes is required), 40 c.c. of *N*-oxalic acid are added and the mixture is further heated for 2 minutes after the noticeable evolution of carbon dioxide has ceased. 2*N*-Sulphuric acid (20 c.c.) and 10% potassium iodide solution (10 c.c.) are then added, together with a fragment of porous pot. The mixture is once more vigorously boiled until the

liberated iodine has been almost completely expelled and th solution is of a pale straw colour (about 15 minutes). This colou is discharged by the cautious addition of $N/20$-sodium thiosulphat the mixture immediately diluted to about 100 c.c., 30 c.c. of 2N sodium carbonate are added, and the still acid solution is treate with a quantity of solid sodium bicarbonate about 1 g. in excess that required to render it neutral to litmus. The mixture is warme to 35—40° and titrated with $N/10$-iodine in presence of starc solution until the blue colour is permanent.

Appended is a list of some of the results obtained with arsenic products of various types. The figures themselves have not bee specially selected and are in all cases duplicate determinations mad on the same sample in the ordinary course of work.

Substance analysed.	As% found.	As% calc
Cacodylic acid	54·5, 54·4	54·3
3-Amino-4-hydroxyphenylarsenious oxide hydrochloride ($1H_2O$)	29·8, 29·8	29·6
Phenylarsinic acid	37·2, 37·3	37·1
p-Tolylarsinic acid	34·8, 34·7	34·7
p-Benzarsinic acid	30·6, 30·5	30·5
p-Arsanilic acid	34·5, 34·6	34·6
3-Nitro-4-hydroxyphenylarsinic acid	28·5, 28·7	28·5
3-Amino-4-hydroxyphenylarsinic acid	31·9, 32·0	32·2
3-Acetylamino-4-hydroxyphenylarsinic acid	27·3, 27·4	27·3
3-Carbethoxyamino-4-hydroxyphenylarsinic acid	24·6, 24·8	24·6
2 : 2′-Dihydroxydiphenylcarbamide-5 : 5′-diarsinic acid	30·6, 30·4	30·5
Sodium *N*-phenylglycineamide-*p*-arsinate (anhydrous tryparsamide)	25·5, 25·4	25·3

	As% found.	As% found by Cariu method.
3 : 3′-Diamino-4 : 4′-dihydroxyarsenobenzene hydrochloride (salvarsan)	30·0, 30·1	30·05
Sodium 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene-*N*-methylenesulphoxylate (neo-salvarsan)	20·1, 20·2	20·1

RESEARCH LABORATORY, MESSRS. MAY AND BAKER, LTD.
WANDSWORTH, S.W. 18. [*Received, May 20th,* 1925.]

NOTES.

Lithium Arc Spectrum for Polarimetric Use. By PERCY CORLET AUSTIN.

BY introducing lithium carbonate into the arc produced betwee carbon, copper, or silver electrodes and using a direct-vision spectr scopic eyepiece of high dispersive power it is possible to read extin tions quite easily, not only for the red line at $\lambda = 6708$ Å. togeth

ith the sodium line at $\lambda = 5893$ Å (Hunter, J., 1924, **125**, 1401), ut also for the orange line at $\lambda = 6104$ Å, the blue line at $\lambda = 602$ Å., and sometimes even the green line at $\lambda = 4972$ Å; but his is much weaker than the others and of comparatively small nportance. The red line is very strong and persistent, whilst the lue line is a valuable addition to the list of lines in common use in neasurements of optical rotatory dispersion, since it lies in the rather ide gap between the dark blue cadmium line at $\lambda = 4678$ Å. and the ercury line at $\lambda = 4359$ Å. Moreover, it is brighter and more asily read than the dark blue cadmium line, when this is produced n an open arc between electrodes of a cadmium–silver alloy.

The red and blue lines of lithium are widely separated from each ther and can be read with sufficient accuracy to enable them to erve as standards, which are independent of the usual mercury nes, in calculating the constants of Drude's equation. The most atisfactory results were obtained with copper electrodes at right ngles to each other. The top of the vertical (positive) pole is bound ith thin copper wire to retain a small quantity of a paste of lithium arbonate and water, and a current of 4·5 amperes is used. The lue copper lines are too weak to interfere with the readings of the lue lithium line.—Westminster Training College, 130 Horse-erry Road, S.W. 1. [*Received, June 16th*, 1925.]

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otassium Antimonoxalate. By Leslie Henry Alfred Holmes and Eustace Ebenezer Turner.

RELIMINARY investigation of the antimonoxalates, which it was oped to resolve into optically active forms, has shown that ney are too unstable for the work in view. The potassium salt, or example, is described by different authors as having x, 2, 3, $3\frac{1}{2}$, $4\frac{1}{2}$, or 6 mols. of water of crystallisation (Hofmann, "Lexikon er anorganischen Verbindungen," Vol. I, 2nd half, 1237; Beilstein, Handbuch," 4th ed., Vol. II, 521).

The potassium salt has been prepared by slowly adding freshly-ecipitated antimonious oxide to a boiling saturated solution of otassium hydrogen oxalate, filtering, and allowing to cool: it parated as star-shaped clusters of needles, which were once crystallised from water below 50° (at or above this temperature was hydrolysed by water), and air-dried. The water of crystal-ation was not completely removed even in a vacuum at 140°, nd the determination of water was effected by ignition in a tube, c. (Found: K, 21·6; Sb, 22·5; C_2O_4, 49·2; H_2O, 6·8. $_3Sb(C_2O_4)_3,2H_2O$ requires K, 21·8; Sb, 22·35; C_2O_4, 49·15; $_2O$, 6·7%).

It is probable that previous workers overlooked the extreme unstable nature of the salt, and were dealing with impure specimen since it is unlikely that they would have obtained higher hydrat than that now described, which separated at low temperatures.

The expense of this work was met by a grant for which the autho are indebted to the Research Fund Committee of the Society.-

East London College, University of London. [*Received, Jun 4th*, 1925.]

A Simplified Method of Micro-combustion: the Micro-Dennste Method. By Casimir Funk and Stanislas Kon.

Some of the disadvantages of Pregl's method of microanalysis ha been overcome by Dubsky (see Houben-Weyl, "Methoden d Organischen Chemie," II. ed.), but the apparatus required is som what complicated. We have devised a simple and accurate proce by an adaptation of Dennstedt's method. The combustions a carried out in a pyrex tube, 43 cm. long, of the usual Pregl patter but fitted with an inner tube 22·5 cm. in length, of which 13·5 cr are inserted into the tube, and a diffusion stopper providing double supply of oxygen. The filling consists of a platinum conta "star," 6 cm. long, and three boats, 7·5 cm. long, one containi molecular silver and the others lead peroxide and red lead. T tube is heated in a Dubsky furnace terminated by a "regenerati block" kept at 150—170°; the burners are arranged as in t Dennstedt process, so that the contact star can be heated to redne while the portion of the tube containing the absorbents is kept about 320° with the aid of the tubular burner. Three Blum absorption tubes, each weighing 14—17 g. when full, are use filled as recommended by Dubsky; these tubes must always used in the same direction. A bubble-counter is attached to t third tube. The capillary rubber tubing used for all connexions specially treated, and the absorption tubes are cleaned and weighe according to Pregl's directions. It is advisable not to wipe t stoppers after a combustion to avoid the risk of removing sm traces of vaselin. The absorption tubes are weighed filled wi oxygen and should be refilled with dry oxygen if not used for day or more.

A newly-fitted combustion tube is burned out in a stream oxygen for 1½ hours. A small platinum boat containing t substance to be analysed (5—9 mg.) is placed in the inner tube the combustion tube, the double oxygen supply carefully adjuste and the combustion carried out as described by Dennstedt. It particularly important to maintain a sufficiently rapid outer strea of oxygen to prevent backward diffusion of the combustion produc

especially when dealing with volatile substances. The combustion takes 40—50 minutes, including the time (20 minutes) required to drive off the water formed; the absorption tubes are then detached, and weighed after 20 minutes.

The following precautions are essential: (1) a sufficient supply of oxygen must be maintained, the outer stream at the rate of two bubbles a second with a bubble-counter 1 mm. in diameter; (2) a good analysis can be obtained only after a satisfactory blank or a successful combustion. Otherwise the process requires no special care. The progress of the combustion can be watched so that any irregularity is noticed at once, the filling of the tube is simple, and the large absorption tubes do not require refilling for a considerable time.

We obtained consistently high results in the estimation of nitrogen by Pregl's method until we placed the layer of reduced copper at the end of the tube as in Dubsky's process; this arrangement obviated the dissociation of the carbon dioxide into carbon monoxide and oxygen. A very slow stream of carbon dioxide generated in a Kipp apparatus was maintained throughout the combustion; and no difficulty was experienced in getting air-free carbon dioxide when Pregl's directions for the filling of the Kipp apparatus were carefully followed.—STATE SCHOOL OF HYGIENE, WARSAW, POLAND. [*Received, April 15th*, 1925.]

CCXXXIII.—*Arylselenoglycollic Acids.*

By GILBERT T. MORGAN and WILLIAM HENRY PORRITT.

ARYLSELENOGLYCOLLIC acids are obtainable by the following process, which avoids the use of hydrogen selenide and is of general application. The first step, due to Taboury (*Bull. Soc. chim.*, 1903, **29**, 761), depends on the interaction of elemental selenium and a magnesium aryl bromide.

The additive product of the Grignard reagent and selenium is decomposed with ice and hydrochloric acid, and the arylselenomercaptan, extracted as alkali salt from its ethereal solution, is condensed with sodium chloroacetate in aqueous alcoholic solution. The process is summarised in the following scheme:

$$\text{Aryl·MgBr} \longrightarrow \text{Aryl·Se·MgBr} \longrightarrow \text{Aryl·SeH}.$$
$$\text{Aryl·SeNa} + \text{CH}_2\text{Cl·CO}_2\text{Na} = \text{Aryl·Se·CH}_2\text{·CO}_2\text{Na} + \text{NaCl}.$$

During its extraction with aqueous alkali 15—20% of the selenomercaptan undergoes aerial oxidation to the corresponding diaryl diselenide, Aryl·Se·Se·Aryl.

The arylselenoglycollic acids (yields 20—25%), when liberated

by mineral acids from their alkali salts, are well-defined, colourless solids, easily soluble in organic media, crystallising from hot water on account of their more sparing solubility in the cold solvent.

In general stability, the arylselenoglycollic acids resemble their sulphur analogues; they melt without decomposition and are not attacked by boiling mineral acids. Unlike the acids of the sulphur series, however, these selenium derivatives do not exhibit any marked tendency towards ring formation under the influence of chlorosulphonic acid at temperatures ranging from −5° to 40°. No seleno-indoxylic substances are produced and the products isolated resemble the decomposition products of the dichlorides of the arylselenoglycollic acids. This observation indicates that the chlorosulphonic acid contributes chlorine to the side chain, which radical subsequently undergoes complex condensation. That the valency of the selenium tends to increase is shown by the formation of crystalline chloro- and bromo-additive products on introducing these halogens into chloroform solutions of the arylselenoglycollic acids. The additive products of bromine are of two types, respectively yellow and red in colour, corresponding to the di- and tetra-bromides. They are easily hydrolysed with the formation of brownish-red oils, a complex change also occurring with the dihalogenides of the arylthioglycollic acids (Pummerer, *Ber.*, 1909, **42**, 2275).

Acidified permanganate solutions are decolorised by the arylselenoglycollic acids, probably with the formation of selenones. With 25% hydrogen peroxide in glacial acetic acid solution, the acids undergo direct oxidation with considerable evolution of heat to furnish well-defined, crystallisable arylselenoxyglycollic acids, Aryl·Se·O·CH_2·CO_2H (yields 95%).

Excess of hydrogen peroxide produces no further oxidation, although potassium permanganate is discoloured. This behaviour towards oxidising agents is similar to that of the aryl disulphides and thiodiglycollic acid (Gazdar and Smiles, J., 1908, **93**, 1833; Hinsberg, *Ber.*, 1908, **41**, 2836).

The arylselenoglycollic acids are very resistant to nitric acid and in Carius determinations the temperature must be maintained at 250° for several hours; they develop characteristic colours with concentrated sulphuric acid, the tint varying with the nature of the aryl radical present.

Both the arylseleno- and arylselenoxy-acids form soluble alkali and ammonium salts, the latter being readily dissociated. The alkali salts of the seleno-acids are stable towards alkali fusion at 250°. The silver salts of both series are only very slowly affected by light.

Experimental.

I. *Arylselenoglycollic Acids.*

1. *Phenylselenoglycollic Acid*, $C_6H_5{\cdot}Se{\cdot}CH_2{\cdot}CO_2H$.—Twenty g. of finely powdered selenium were added slowly to magnesium phenyl bromide, from 39 g. of bromobenzene and 6 g. of magnesium in dry ether; brisk effervescence occurred and the mixture was cooled in ice, the reaction being afterwards completed by warming on a water-bath. The cooled mixture was poured on to ice and hydrochloric acid, when a small quantity of hydrogen selenide was evolved and red selenium separated. The ethereal layer was extracted rapidly with 7 g. of caustic potash (100%) in 60 c.c. of water, and to the aqueous solution were added 100 c.c. of alcohol and a solution of sodium chloroacetate (from 6·7 g. of sodium carbonate and 11·8 g. of monochloroacetic acid). Heat was generated and the sodium salt of the glycollic acid was precipitated as a white powder. The reaction was completed on a water-bath, and on concentrating the solution to half its bulk, sodium phenylselenoglycollate crystallised in pinkish-white plates. *Phenylselenoglycollic acid* separated as a pale yellow oil on adding hydrochloric acid to an aqueous solution of its colourless, recrystallised sodium salt. This acid dissolved in a large quantity of boiling water, separating therefrom as a colourless oil, b. p. 160°/750 mm., which became crystalline on standing for several days; m. p. 40°. The potassium salt crystallised in colourless plates with a silvery lustre (Found: C, 44·6; H, 3·7; Se, 36·7. $C_8H_8O_2Se$ requires C, 44·65; H, 3·7; Se, 36·7%).

Phenylselenoglycollic acid, which dissolved in the majority of organic solvents, was only sparingly soluble in cold water; its aqueous solution was acid to litmus. With concentrated sulphuric acid, it developed a deep purple coloration; its bright green copper salt was insoluble in water.

2. p-*Bromophenylselenoglycollic Acid*, $C_6H_4Br{\cdot}Se{\cdot}CH_2{\cdot}CO_2H$.—The condensation of 13·3 g. of selenium and the Grignard reagent from 40 g. of *p*-dibromobenzene and 4 g. of magnesium powder in dry ether was completed on a water-bath and the cooled product subsequently decomposed with ice and hydrochloric acid. The resulting *p*-bromophenylselenomercaptan was extracted with 5 g. of caustic potash and 50 c.c. of water, and to the alkaline solution 50 c.c. of alcohol and an aqueous solution of sodium chloroacetate from 8 g. of monochloroacetic acid were added. After warming on the water-bath for 30 minutes, the solution, on cooling, deposited sodium *p*-bromophenylselenoglycollate slightly pink in colour. The free *acid* crystallised from hot water in colourless, lustrous needles, m. p. 127° (Found: C, 32·7; H, 2·4; Se, 26·9; Br, 27·2.

$C_8H_7O_2BrSe$ requires C, 32·2; H, 2·3; Se, 26·9; Br, 27·2%). *p*-Bromophenylselenoglycollic acid dissolved readily in most organic solvents, but was only sparingly soluble in cold water to a solution having an acid reaction to litmus. The silver salt was only slowly decomposed by light; the green copper salt was insoluble. A deep brown colour was developed in concentrated sulphuric acid.

3. p-*Tolylselenoglycollic acid*, $CH_3{\cdot}C_6H_4{\cdot}Se{\cdot}CH_2{\cdot}CO_2H$, prepared by the general method from magnesium *p*-tolyl bromide, separated from acidified solutions of its recrystallised sodium salt. When crystallised from hot water, this acid was obtained in well-defined lustrous, acicular prisms melting at 98° and giving a carmine-red coloration with concentrated sulphuric acid (Found: C, 47·1; H, 4·4; Se, 34·4. $C_9H_{10}O_2Se$ requires C, 47·2; H, 4·4; Se, 34·5%).

The alkali and ammonium salts were colourless, crystalline substances soluble in water; the green copper salt was insoluble.

4. *α-Naphthylselenoglycollic acid*, $C_{10}H_7{\cdot}Se{\cdot}CH_2{\cdot}CO_2H$, prepared by the general method from magnesium α-naphthyl bromide, separated from acidified solutions of its sodium salt, and as an oil from hot water. On remaining in a vacuum desiccator for 3 weeks the oil crystallised to a product, m. p. 54°, which gave a green coloration in concentrated sulphuric acid (Found: C, 54·3; H, 3·7; Se, 29·7. $C_{12}H_{10}O_2Se$ requires C, 54·3; H, 3·8; Se, 29·8%).

II. *Arylselenoxyglycollic Acids.*

1. p-*Bromophenylselenoxyglycollic acid*, $C_6H_4Br{\cdot}SeO{\cdot}CH_2{\cdot}CO_2H$, separated in well-defined, colourless needles, m. p. 187°, when 6 c.c. of hydrogen peroxide (25%) were added to 2·9 g. of *p*-bromophenylselenoglycollic acid dissolved in glacial acetic acid, the solution being cooled to moderate the reaction (Found: C, 40·0; H, 2·2; Se, 25·5. $C_8H_7O_3BrSe$ requires C, 40·0; H, 2·25; Se, 25·5%).

p-Bromophenylselenoxyglycollic acid, which dissolved in chloroform or alcohol, was less soluble in ether than the selenoglycollic acid. It dissolved only very slightly in cold, but more so in hot water. The alkali and ammonium salts were colourless and soluble. The pale blue copper salt was insoluble.

2. p-*Tolylselenoxyglycollic acid*, $C_6H_4Me{\cdot}SeO{\cdot}CH_2{\cdot}CO_2H$, produced as in the preceding preparation, separated from glacial acetic acid in colourless crystals, m. p. 165° (Found: C, 44·0; H, 4·0; Se, 32·5. $C_9H_{10}O_3Se$ requires C, 44·1; H, 4·1; Se, 32·2%).

Aqueous or acetic acid solutions of the foregoing arylselenoxy acids liberated iodine from aqueous potassium iodide.

III. *Halogenides of Arylselenoglycollic Acids.*

1. p-*Tolylselenoglycollic Acid Dibromide*, $C_6H_4Me{\cdot}SeBr_2{\cdot}CH_2{\cdot}CO_2H$.—A solution of 2·29 g. of *p*-tolylselenoglycollic acid (m. p. 98°) in 25 c.c. of dry chloroform was treated with 1·6 g. (1 mol.) of bromine and left in a vacuum desiccator. The dibromide separated in clusters of golden-yellow needles, which decomposed between 90° and 100° with evolution of bromine (Found: Br, 40·9; Se, 20·3. $C_9H_{10}O_2Br_2Se$ requires Br, 41·1; Se, 20·3%).

An aqueous solution of potassium iodide reacted with the dibromide, liberating iodine and regenerating a quantity of the original acid together with a proportion of the corresponding selenoxy-acid. The dibromide was unstable in moist air and was easily hydrolysed, giving brownish-red oils of complex constitution.

2. p-*Tolylselenoglycollic acid tetrabromide*,

$$C_6H_4Me{\cdot}SeBr_4{\cdot}CH_2{\cdot}CO_2H,$$

prepared in a similar manner to that described above by the addition of 3·8 g. of bromine (20% in excess of 2 mols.) to 2·29 g. of *p*-tolylselenoglycollic acid dissolved in dry chloroform, separated in small, scarlet needles which readily decomposed on warming (Found: Br, 58·3; Se, 14·4. $C_9H_{10}O_2Br_4Se$ requires Br, 58·3; Se, 14·4%). The tetrabromide was readily hydrolysed and liberated iodine from an aqueous solution of the acid.

3. p-*Bromophenylselenoglycollic acid dibromide*,

$$C_6H_4Br{\cdot}SeBr_2{\cdot}CH_2{\cdot}CO_2H,$$

prepared as above from 2·94 g. of *p*-bromophenylselenoglycollic acid and 1·6 g. of bromine, formed golden-yellow crystals decomposing at 120—130° with evolution of bromine (Found: Br, 52·8; Se, 17·4. $C_8H_7O_2Br_3Se$ requires Br, 52·9; Se, 17·4%).

4. p-*Bromophenylselenoglycollic acid tetrabromide*,

$$C_6H_4Br{\cdot}SeBr_4{\cdot}CH_2{\cdot}CO_2H,$$

prepared from 2·94 g. of *p*-bromophenylselenoglycollic acid and 3·8 g. of bromine in dry chloroform, formed scarlet needles which decomposed on warming with evolution of bromine (Found: Br, 65·0; Se, 12·8. $C_8H_7O_2Br_5Se$ requires Br, 65·15; Se, 12·9%).

The authors desire to express their thanks to the Government Grant Committee of the Royal Society and to the University of Birmingham Research Committee for grants which have helped to defray the expense of this investigation.

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CCXXXIV.—*Aromatic Derivatives of Germanium.*

By Gilbert T. Morgan and Harry Dugald Keith Drew.

When germanium tetrabromide is treated with a large excess of magnesium phenyl bromide (36 mols.) it yields *germanium tetraphenyl* or *tetraphenylgermane*, $Ge(C_6H_5)_4$, *triphenylgermanium bromide* $Ge(C_6H_5)_3Br$, and the less phenylated germanium bromides $Ge(C_6H_5)_2Br_2$ and $Ge(C_6H_5)Br_3$. The first two products are readily separated, but the latter pair, which do not solidify when mixed, have been identified by the isolation of their hydrolytic products.

Hexaphenyldigermane, $(C_6H_5)_3Ge{\cdot}Ge(C_6H_5)_3$, has not been detected among the products of the Grignard reaction, so that under these experimental conditions there is little or no tendency for junction of two atoms of the metal (compare with tin and lead), but the compound is readily prepared by the action of sodium on triphenylgermanium bromide.

$$2GePh_3Br + 2Na = Ph_3Ge{\cdot}GePh_3 + 2NaBr.$$

The production of tetraphenylgermane and hexaphenyldigermane completes the following series :—

	CPh_4.	$SiPh_4$.	$GePh_4$.	$SnPh_4$.	$PbPh_4$.
M. p.	272°	233°	230—231°	225—226°	224—225°
	C_2Ph_6.	Si_2Ph_6.	Ge_2Ph_6.	Sn_2Ph_6.	Pb_2Ph_6.
M. p.	145—147°*	354°	340°	237°	155°*

* These abnormally low melting points are due to dissociation.

Hexaphenyldigermane when examined in dilute benzene solution shows no recognisable tendency to dissociation.

On hydrolysis the solid triphenylgermanium bromide yields *triphenylgermanium oxide*, $(C_6H_5)_3Ge{\cdot}O{\cdot}Ge(C_6H_5)_3$, corresponding with the silicon compound, $Ph_3Si{\cdot}O{\cdot}SiPh_3$. The analogue, $Ph_3Ge{\cdot}OH$, of triphenylsilicon hydroxide was not isolated.

Hydrolytic Products from Diphenylgermanium Dibromide and Phenylgermanium Tribromide.—When only 5 molecular proportions of magnesium phenyl bromide are employed to one of germanium tetrabromide, there is no formation of tetraphenylgermane but the product contains a mixture of mono-, di-, and tri-phenylgermanium bromides.

Diphenylgermanium dibromide yielded on hydrolysis two well-defined complex substances derived by dehydration from the hypothetical dihydroxide or diol, $(C_6H_5)_2Ge(OH)_2$. These products

which have considerable capacity for crystallisation, are *trianhydrotetrakisdiphenylgermanediol*,

$$HO{\cdot}GePh_2{\cdot}O{\cdot}GePh_2{\cdot}O{\cdot}GePh_2{\cdot}O{\cdot}GePh_2{\cdot}OH$$

(I), m. p. 149°, and *tetra-anhydrotetrakisdiphenylgermanediol*,

$$O<\begin{matrix}GePh_2{\cdot}O{\cdot}GePh_2\\GePh_2{\cdot}O{\cdot}GePh_2\end{matrix}>O$$

(II), m. p. 218°.

The formation of these complicated anhydro-compounds recalls the results obtained by Kipping and his collaborators (J., 1912, **101**, 2108, 2125; 1914, **105**, 484) on hydrolysing diphenylsilicon dichloride, when the diol $Ph_2Si(OH)_2$ and four anhydrides were identified. The two silicon derivatives corresponding with formulæ I and II melt respectively at 128—129° and 200—201°. Diphenylgermanium dibromide also undergoes hydrolysis to an insoluble amorphous substance (p. 1765), from which it is regenerated by concentrated hydrobromic acid.

Owing to this tendency to form anhydrides it is obvious that hydrolysis of a mixture of diphenylgermanium dibromide and phenylgermanium tribromide might lead to an anhydro-diol derived from more than one of the reacting bromides. This anticipation was realised by the isolation of a substance (m. p. 275°) having a composition and molecular weight approximating to $Ge_5(C_6H_5)_8O_6$, which may be regarded as a combination of $3GePh_2O$ with $GePhO{\cdot}O{\cdot}GePhO$, these oxides being derived from the hydrolysis of diphenylgermanium dibromide and phenylgermanium tribromide, respectively. This product, which arises apparently from a chance condensation of the two different oxy-compounds, was only obtained in one experiment.

The hydrolysis of phenylgermanium tribromide leads to *phenylgermanonic* or *germanibenzoic acid*, a colourless uncrystallised product soluble in aqueous caustic alkalis. Its properties in regard to degree of hydration vary with the experimental conditions of its preparation and isolation. In all probability its composition varies within the limits $C_6H_5{\cdot}GeO{\cdot}OH$ and $C_6H_5{\cdot}GeO{\cdot}O{\cdot}OGe{\cdot}C_6H_5$ (III) and the analytical numbers approximate to an intermediate complex formula still containing hydroxyl groups. Phenylgermanonic acid or germanibenzoic acid therefore comes into line with silicobenzoic acid and its analogues, which have been shown conclusively by Kipping and his collaborators (J., 1914, **105**, 679; 1915, **107**, 459) to consist of mixtures of condensation products varying in composition with the conditions of hydrolysis of the halogenated silicanes.

The foregoing results obtained with oxygenated phenylgermanium compounds indicate that the reactions of these substances are similar

to those of the oxyarylsilicon derivatives but of a somewhat simpler type with less tendency to the formation of syrups, colloids and infusible mixtures. In this respect germanium forms a link between silicon and tin, and the germanium atom should exhibit a tetrahedral distribution of valencies.

Experimental.

I. *Interaction of Germanium Tetrabromide with a Large Excess of Magnesium Phenyl Bromide.*

1. The Grignard reagent from 5·7 g. of magnesium, 30·2 g. of bromobenzene, and 120 c.c. of ether (36 mols. PhMgBr) was added to 2·1 g. of germanium tetrabromide in 75 c.c. of ether, and the mixture heated for 2 hours. The dark orange-yellow liquid was poured on to ice and acidified with hydrobromic acid, when a creamy white powder remained consisting of *tetraphenylgermane* (0·8 g. or 40%). The ethereal filtrate and extracts, dried over sodium sulphate and concentrated, yielded 0·5 g. of *triphenyl germanium bromide;* the final mother-liquor containing the less phenylated products was worked up as described on p. 1765.

2. During the action of less Grignard reagent (8 mols. PhMgBr) on 4·4 g. of germanium tetrabromide in 25 c.c. of pure chloroform (Boots') heat was generated. The resulting liquid, after being warmed on the water-bath for 1½ hours, was treated as above and yielded 0·93 g. of tetraphenylgermane (22%) and 1·1 g. of triphenyl germanium bromide (26%), the separation of the latter being hastened by adding petroleum (b. p. 60—80°). The ether-petroleum mother-liquors, distilled in steam to remove diphenyl, left a semi-solid yellowish-brown mass which after trituration left 0·4 g. of colourless crystalline *triphenylgermanium oxide*. The oily bromide were worked up as on p. 1765, whereas the aqueous layer from the hydrolysis of the Grignard product by ice deposited gradually a small amount of *phenylgermanonic* or *germanibenzoic acid*.

Tetraphenylgermane (*Germanium tetraphenyl*), $GePh_4$, crystallised from petroleum (b. p. 60—80°) in lustrous, refractive, transparent, prismatic needles, colourless in small quantities, cream-white in bulk. Very stable on heating, it melted at 230—231° and could be volatilised without decomposition (Found: C, 75·4; H, 5·6; Ge, 18·5. $C_{24}H_{20}Ge$ requires C, 75·7; H, 5·3; Ge, 19·0%).

Tetraphenylgermane was insoluble in water, sparingly soluble in ether, light petroleum, or cold acetone, and dissolved more readily in benzene, separating therefrom in acicular prisms. Boiling aqueous caustic alkalis had no effect on this substance; it was insoluble in cold concentrated sulphuric acid, but on warming sulphonation occurred destructively with elimination of phenyl

groups. Fuming nitric acid or a mixture of nitric and sulphuric acids caused nitration and oxidation with evolution of nitrous fumes.

Triphenylgermanium bromide, $GePh_3Br$, formed large, colourless, transparent, six-sided, refractive, prismatic needles or small, compact prisms. Insoluble in water but somewhat readily soluble in ordinary organic media, it was best crystallised from petroleum (b. p. 40—80°); it melted at 138° to a colourless liquid (Found: C, 56·6; H, 4·1; Br, 20·7. $C_{18}H_{15}BrGe$ requires C, 56·3; H, 3·9; Br, 20·8%).

Triphenylgermanium bromide became hydrolysed superficially to its oxide by boiling water or by warm aqueous caustic alkalis. It arose as a by-product in the preceding preparations, but became the chief product when five molecular proportions of the Grignard reagent were employed to one of germanium tetrabromide. When 0·3 g. of the latter substance were used, the ethereal solution, after heating on the water-bath and subsequent treatment with ice and hydrobromic acid, yielded, on concentration of the ether layer, 2·5 g. (or 27%) of triphenylgermanium bromide. The residual oil was then treated with aquo-alcoholic silver nitrate, filtered from silver bromide, and the filtrate evaporated and distilled in steam, when diphenyl and *o*-nitrophenol were removed in the distillate. The non-volatile semisolid residue was fractionated from boiling petroleum (b. p. 60—80°) and from cold ether, when the following crystalline substances were separated: (i) a colourless compound (0·7 g.) melting at 275°, practically insoluble in cold ether or light petroleum and only sparingly soluble in the latter on warming (see pp. 1761, 1767); (ii) *tetra-anhydrotetrakisdiphenylgermanediol* (0·2 g.) melting at 218°, more soluble in ether or petroleum (see p. 1761, 1766); (iii) an orange-yellow substance (0·1 g.) melting from 106° to 112°, very soluble in organic solvents or in water. This product (C, 51·3; H, 4·5%) contained no germanium and did not depress the melting point of ordinary *p*-nitrophenol (C, 51·8; H, 3·6%), but unlike the latter it was intensely yellow and more soluble in cold water. Being formed from phenylated germanium derivatives and silver nitrate in the absence of mineral acids, it may consist in part of an *aci*-form of *p*-nitrophenol. In addition to these solid products there was a considerable proportion of uncrystallisable germaniferous material which was worked up subsequently as described on p. 1766.

Triphenylgermanium Oxide, $Ph_3Ge{\cdot}O{\cdot}GePh_3$.—An alcoholic solution of triphenylgermanium bromide was boiled with silver nitrate, filtered from silver bromide, and diluted with water, when the oxide was obtained in quantitative yield. This product crystallised from hot petroleum (b. p. 60—80°) in transparent, colourless

prisms melting to a colourless liquid at 182—183°; it separated from ethyl acetate in thin, six-sided plates (Found: C, 69·2; H, 4·9; Ge, 23·2. $C_{36}H_{30}OGe_2$ requires C, 69·35; H, 4·85; Ge, 23·2%).

In organic media triphenylgermanium oxide was more soluble than tetraphenylgermane but less so than triphenylgermanium bromide; it was unattacked by 50% aqueous caustic potash, but was reconverted quantitatively into triphenylgermanium bromide by hydrobromic acid (*d* 1·45).

Hexaphenyldigermane, $Ph_3Ge{\cdot}GePh_3$. — Triphenylgermanium bromide (3 g.) dissolved in 37 c.c. of dry xylene was heated for 3 hours with excess of " molecular " sodium. The filtered solution deposited on cooling 2·2 g. of hexaphenyldigermane, and a further amount was obtained on concentration. The final filtrate contained a small quantity of the more soluble triphenylgermanium oxide arising as a by-product.

Hexaphenyldigermane separated from hot benzene in large, colourless, transparent cubes crumbling into powder on exposure to air: loss of benzene at 100° = 24·3%, corresponding with 3 mols. of C_6H_6. It was sparingly soluble in cold but more soluble in hot chloroform, separating therefrom in colourless micro-crystals, m. p. 340° [Found: C, 70·8, 70·7; H, 5·1, 5·3; Ge, 23·5; *M*, ebullioscopic in benzene, 566 ($c = 0·595$), 560 ($c = 1·328$). $C_{36}H_{30}Ge_2$ requires C, 71·2; H, 5·0; Ge, 23·85%; *M*, 606·8].

Hexaphenyldigermane was insoluble in boiling aqueous caustic soda, but on boiling with alcoholic silver nitrate a slight blackening occurred owing to liberation of silver.

Phenylgermanonic Acid (*Germanibenzoic Acid*, p. 1761).—The aqueous mother-liquors from the hydrolysis of the Grignard mixture slowly deposited a white, colloidal precipitate, which was purified for analysis by redissolving in aqueous caustic soda, the filtered solution being then acidified, when the white, amorphous powder separated and was dried at 100° (Found: C, 39·9; H, 3·2. The simplest formula, $C_6H_6O_2Ge$, requires C, 39·5; H, 3·3%).

From concentrated solutions of its sodium salt, phenylgermanonic acid separated at once (hydrogel form), but in dilute solutions it remained dissolved (hydrosol condition) and separated only after several weeks.

II. *Interaction of Germanium Tetrabromide and Magnesium Phenyl Bromide* (5 *mols.*).

A Grignard solution, prepared from 48·4 g. of bromobenzene (5 mols.), 9·1 g. of magnesium, and 200 c.c. of ether, was added slowly to an ice-cold solution of 24·5 g. (1 mol.) of germanium tetrabromide in 100 c.c. of ether, moisture and carbon dioxide being

excluded. The heavy colourless oil which separated persisted after heating on the water-bath. The cooled mixture was decomposed by ice and 50 c.c. of hydrobromic acid (*d* 1·45), when the crackling sound produced by the hydrolysis of germanium tetrabromide showed that this substance was not completely attacked even by excess of Grignard reagent. The solution was extracted with ether and the mixed ethereal extracts were dried over sodium sulphate. The aqueous layer, which gave no precipitate of phenylgermanonic acid (germanibenzoic acid) either when left or when partially neutralised, contained no other organic derivatives of germanium.

The ethereal extract, concentrated to a small bulk, gave 9 g. (37·5%) of *triphenylgermanium bromide.*

The residual oil, which contained a complex mixture of triphenylgermanium bromide, the less phenylated germanium bromides, and chiefly diphenylgermanium dibromide together with diphenyl and traces of bromobenzene, was dissolved in 150 c.c. of alcohol and added to 20 g. of silver nitrate in 100 c.c. of alcohol and 40 c.c. of water, when a dark brown precipitate separated. The mixture was heated under reflux for an hour and the alcoholic filtrates (A) separated from a black precipitate (B). This precipitate B, which consisted mainly of silver bromide but contained some organic germanium compound, was boiled with ammonia (*d* 0·88),* when a black residue remained which was extracted successively with aqueous sodium thiosulphate and dilute nitric acid, leaving 1·5 g. of a white, amorphous organic germanium compound. This substance melted partly at 260° and was insoluble in organic solvents, aqueous alkalis or ammonia; it was converted by hydrobromic acid into an oily bromide, from which the original amorphous substance was recovered by the action of water. This uncrystallisable product was also obtained by the hydrolysis of the oily bromide from tetra-anhydro-tetrakisdiphenylgermanediol, m. p. 218°.

The alcoholic filtrate A was evaporated and the oily residue distilled in steam, when diphenyl and *o*-nitrophenol passed over. The residue, a solid of pitchy consistence, was dissolved in ether and the yellow solution filtered and concentrated until an orange-yellow, semi-crystalline mass separated. This product, after extraction with cold petroleum (b. p. 80—100°) to remove diphenyl and other more soluble impurities, furnished 5 g. of an almost

* The ammoniacal filtrate deposited on cooling lustrous spangles of silver bromide having a highly refractive reflex. This product was an insensitive form of the bromide, for it retained its bright metallic lustre after months of exposure to light. The ammoniacal liquor, which contained traces of organic derivatives of germanium, had the property of converting more yellow silver bromide to this insensitive form, the spangles separating at the surface of the solution.

colourless mixture of organic germanium derivatives now free from bromine. Repeated solution of this mixture in ethyl acetate followed by fractional crystallisation and hand-picking of the resulting crystals led to a separation of the following substances :—

1. *Triphenylgermanium oxide*, m. p. 182—183° (see p. 1763), separating from ethyl acetate in thin, rhomboidal or pentagonal plates.

2. *Tetra-anhydrotetrakisdiphenylgermanediol* (Formula II), crystallising in colourless, cubical and prismatic forms, the latter with bevelled and facetted faces. This complex diol was purified by crystallisation from petroleum or ethyl acetate, in which it was readily soluble, and then melted indefinitely at 218° [Found : C, 59·4, 59·1 ; H, 4·25, 4·4. $(C_{12}H_{10}OGe)_x$ requires C, 59·4 ; H, 4·2%.

Fig. 1.

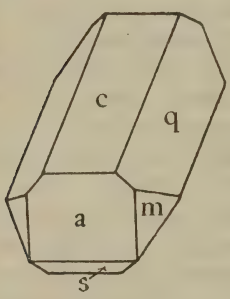
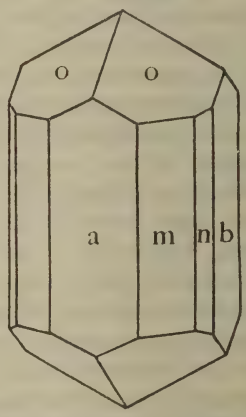


Fig. 2.



Found : by the ebullioscopic method in benzene ($c = 1·48$), M, 905. $(C_{12}H_{10}OGe)_4$ requires M, 970].

3. *Trianhydrotetrakisdiphenylgermanediol* (Formula I), m. p. 149°, obtained in colourless, hexagonal prisms or flattened, rhomboidal crystals with bevelled edges (Found : C, 58·8 ; H, 4·6. $C_{48}H_{42}O_5Ge_4$ requires C, 58·3 ; H, 4·25%).

Crystallographic Examination.

Two of the foregoing substances (Nos. 2 and 3) were kindly examined by Dr. T. V. Barker, who reports as follows :—

Tetra-anhydrotetrakisdiphenylgermanediol (Fig. 1).—The crystals of this substance are monoclinic with the forms $m(110)$, $a(100)$, $q(011)$, $c(001)$ and $s(201)$ developed in the proportions given in Fig. 1. The axial ratios, $a : b : c = 1·491 : 1 : 1·018$, $\beta = 111° 42'$, were computed from the following results given by four crystals.

	m.	*a*.	*q*.	*c*.	*s*.
ϕ.....	0° 0′	0° 0′	68° 21′	*68° 18′	*137° 0′
ρ.....	35 45	90 0	*46 35	90 0	90 0

Optically, the crystals are positive; the axial plane is $b(010)$, and one optic axis is nearly normal to $a(100)$.

Trianhydrotetrakisdiphenylgermanediol (Fig. 2).—The crystals are orthorhombic with the forms $a(100)$, $m(110)$, $n(120)$, $b(010)$, and $o(111)$ developed in the proportions given in Fig. 2. The axial ratios, $a : b : c = 0{\cdot}9539 : 1 : 0{\cdot}5399$, were computed from the following measurements derived from four crystals.

	b.	*n*.	*m*.	*a*.	*o*.
ϕ	0° 0′	27° 50′	*46° 21′	90° 0′	46° 21′
ρ	90 0	90 0	90 0	90 0	*38 2

Optically, the positive acute bisectrix is parallel to the *c*-axis, and the axial plane is *a*.

The Complex Diol melting at 275°.—When recrystallised from ethyl acetate, it separated in large, transparent, colourless prisms melting at 231° and containing solvent of crystallisation. At 140° the loss of weight was 4·45%, corresponding approximately with 2 mols. of diol combined with one of ethyl acetate (theory 3·9%). Crystallised from carbon tetrachloride, the compound melted to a transparent, colourless liquid at 277—278° but rather indefinitely [Found : C, 53·8; H, 3·9; Ge, 33·6; *M*, ebullioscopic in benzene ($c = 1{\cdot}000$), 1003. $C_{48}H_{40}O_6Ge_5$ requires C, 53·6; H, 3·7; Ge, 33·7%; *M*, 1074].

This complex diol was insoluble in water, dilute alcohol, ether, or petroleum and only sparingly soluble in other organic media.

Note on the Analysis of Aromatic Germanium Compounds.

In estimating carbon and hydrogen the combustion was effected entirely with oxygen in a tube containing copper oxide and lead chromate. The oxygenated germanium compounds required very prolonged heating at high temperatures in order to oxidise the last traces of carbon, which otherwise remained in the boat or on the side of the tube as a refractory black material.

For the estimation of germanium the weighed substance was digested during 8 or 10 hours with 18 c.c. of concentrated sulphuric acid (A.R. quality) in a flask with a ground-in air-condenser. The cooled liquid and undissolved germania were washed into a conical flask with 150 c.c. of water, any adherent germania being removed by boiling aqueous sodium carbonate (A.R.). The clear solution was thoroughly saturated with washed hydrogen sulphide and left in the closed flask for a day. The pinkish-white sulphide containing free sulphur and some organic matter was collected on a Gooch crucible with ashless paper filter, and washed successively with 4*N*-sulphuric acid saturated with hydrogen sulphide and aqueous hydrogen sulphide. After drying at 100° the precipitate and the portion

remaining on the filter-paper were converted into germania in separate porcelain crucibles by treatment with dilute and then with concentrated nitric acid. On igniting the crucibles strongly, germania was obtained in a perfectly white condition.

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CCXXXV.—*The Stability of Additive Compounds between Esters and Acids.*

By JAMES KENDALL and JAMES ELIOT BOOGE.

THE parallelism between the electrical conductivity of an acid solution and its catalytic activity in ester hydrolysis formed one of the strongest supports of the Arrhenius ionisation theory in its early stages. More accurate measurements made it evident, however, that direct proportionality between hydrogen-ion concentration and reaction velocity could not be claimed. Other divergences were soon noted; not only did the rate of hydrolysis increase more rapidly than hydrogen-ion concentration, it also increased with the ester concentration. Many investigations have been performed upon ester–acid–water systems to explain these divergences, and several interesting theories—for example, the theory of the catalytic activity of the undissociated molecule and the theory of the anticatalytic effect of water—have been developed. The radiation hypothesis also has been applied to the problem by Lewis and his co-workers, but the mechanism of acid catalysis of ester hydrolysis is still unsolved.

Some advance has been made, nevertheless, in the general recognition of the fact that the concentrations of the reacting molecular species in a solution of this complicated character cannot be directly calculated from its composition. Formation of additive compounds certainly disturbs the stoicheiometric ratios very materially, and inasmuch as it appears most probable that the hydrolysis is effected in steps, with these compounds as intermediate products, it is clearly important to examine their character and stability as thoroughly as possible.

The first direct evidence of the existence of additive compounds between esters and acids was furnished by the present authors in an earlier article (*J. Amer. Chem. Soc.*, 1916, **38**, 1712), in which

xtensive references to previous work will also be found. Thirteen lefinite compounds of the general type R·CO·OR′,HX were isolated, nd it was shown qualitatively that the stability of such compounds n the liquid state increased as the radicals R and R′ were made more lectropositive, or as the radical X was made more electronegative. The most stable compounds were consequently obtained when an *ster of a weak acid* (*e.g.*, ethyl acetate) was paired with a *strong acid* *e.g.*, trichloroacetic acid), but some compound formation was still ndicated even in such an unfavourable system as methyl oxalate–cetic acid.

From the results of this investigation, the general conclusion was drawn that the formation of an ester–acid additive compound onstitutes the first step in ester hydrolysis. The following articles liscuss the stability of these complexes quantitatively, and also xamine the evidence with regard to their dissociation and the ormation of additive compounds of other types in the presence of he third component—water.

The progressive dissociation of ester–acid compounds on addition f water may be postulated as due to three distinct causes. In the irst place, the effect may be purely *diluent*, the equilibrium point n the reaction $R{\cdot}CO{\cdot}OR',HX \rightleftharpoons R{\cdot}CO{\cdot}OR' + HX$ being shifted n the forward direction merely by the diminution in the concen-rations of ester and acid as we proceed from the anhydrous system o a dilute aqueous solution. Secondly, the water may disturb the quilibrium still further by combining with the free acid or ester to orm binary complexes of the type HX,H_2O or $R{\cdot}CO{\cdot}OR',H_2O$. Thirdly, the water may combine with the ester–acid compound to ive a ternary complex of the type $R{\cdot}CO{\cdot}OR',HX,H_2O$.

In order to separate these three factors, as far as is feasible, the roblem has been taken up in stages. First, the extent of the lissociation of certain typical ester–acid compounds into their omponents on fusion has been examined by comparing the freezing-oint depressions induced by addition of free ester, an inert solute benzene), and the active solute water. Next, the extent to which ster–acid compounds are still existent in a dilute solution, when the olvent is inert, has been investigated by determining the freezing-oint depression curves of benzene on addition of ester and of acid, eparately and in company. Binary systems of the types acid–vater and ester–water are then discussed, and the final and most ntricate case of all (the ternary system: ester–acid–water) is thus pproached only after the results of the preceding work have fur-ished useful information as to the most promising methods of ttack.

The Stability of Ester–Acid Compounds on Fusion.

Three compounds are examined in this section, the complexes chosen being those formed by trichloroacetic acid with ethyl acetate benzyl benzoate and methyl succinate respectively. The extent of dissociation in each case is calculated from the form of the freezing-point depression curves of the compound, as indicated in Fig. 1.

This method was first suggested by Bancroft (*J. Physical Chem.* 1899, **3**, 72) and developed in detail by Kremann (*Monatsh.*, 1904 **25**, 1215). Unfortunately, the equations arrived at by Kremann are not free from error (Roozeboom and Aten, *Z. physikal. Chem.* 1905, **53**, 449) and it is important to note that the method is *strictly* applicable only when the heat of dissociation of the complex is zero. Nevertheless, since in mixtures of organic substances heats of dissociation are in general but small, and the stability of a given compound may be regarded as constant over a restricted temperature range, the method may be utilised to give approximately accurate values, the procedure being briefly as follows:

If an additive compound is perfectly stable on fusion, its freezing-point curve on addition of y moles of either component to 100 moles of compound will be given by the equation:

$$-\log_e\left(\frac{100}{100+y}\right)=\frac{Q}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right) \quad . \quad . \quad . \quad \text{(I)}$$

where Q is the molar heat of fusion of the compound in calories, T_0 its absolute temperature of fusion in the pure state, T its absolute temperature of fusion in the solution, and R the gas constant 1·988. If, on the other hand, the percentage dissociation of the pure compound on fusion is x, then addition of y moles of either component to 100 moles of the compound will repress this dissociation to a smaller value x', and we obtain the equation:

$$-\log_e\left(\frac{100-x'}{100+x'+y}\right)=\frac{Q}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right) \quad . \quad . \quad \text{(II)}$$

the graph for which will vary more and more from that given by equation (I), according as x increases. Various trial values may be assumed for x, and the resultant curves compared with that obtained experimentally until accordance is reached.

It remains to show how the "unknowns" in equation (II) may be evaluated. If K is the dissociation constant of the reaction $R{\cdot}CO_2R'$, $HX \rightleftharpoons R{\cdot}CO_2R' + HX$, then we have the two equations

$$\left(\frac{x}{100+x}\right)^2=K\left(\frac{100-x}{100+x}\right) \quad . \quad . \quad . \quad \text{(III)}$$

and

$$\frac{x'(x'+y)}{(100+x'+y)^2}=K\left(\frac{100-x'}{100+x'+y}\right) \quad . \quad . \quad \text{(IV)}$$

ience, as K is known for each assumed value of x, the variation of with y is derived. Q must be determined either calorimetrically, (by calculation) from the form of the freezing-point curve when an ert solute is added. R, of course, is known. The only remaining tor, T_0 (the hypothetical freezing point for the pure compound the absence of dissociation products), is obtained from equation I) by putting $y = 0$, when x' becomes x and T becomes the perimental freezing point.

1. *The Compound Ethyl Acetate–Trichloroacetic Acid.*—This mpound, as obtained by mixing equimolecular quantities of its refully purified components, melted sharply at $-26{\cdot}8°$. A nplified Beckmann type of apparatus was used to determine the ezing-point depression curves of this material on addition of hyl acetate, benzene and water, and in view of the approximate ture of the method and the difficulty of working at low temper- ures and maintaining anhydrous conditions, no attempt was made obtain readings for the freezing-point depression (ΔT) to a eater accuracy than 0·05° in the more dilute, or 0·1° in the more ncentrated solutions. Additions of solute were made by means of Grethan pipette. Compositions are expressed throughout in olecular percentages.

TABLE I.

Freezing-point Depression Curves of the Compound: Ethyl Acetate–Trichloroacetic Acid.

Solutes.						
hyl acetate	Mol. %	4·23	9·55	15·45	22·75	34·5
	$\Delta T°$	0·15	0·60	1·30	2·6	5·5
nzene	Mol. %	3·27	7·74	13·4	21·3	23·2
	$\Delta T°$	0·80	2·0	3·2	5·3	6·0
ater	Mol. %	7·47	15·24	21·3	33·7	
	$\Delta T°$	1·90	3·9	5·5	9·6	

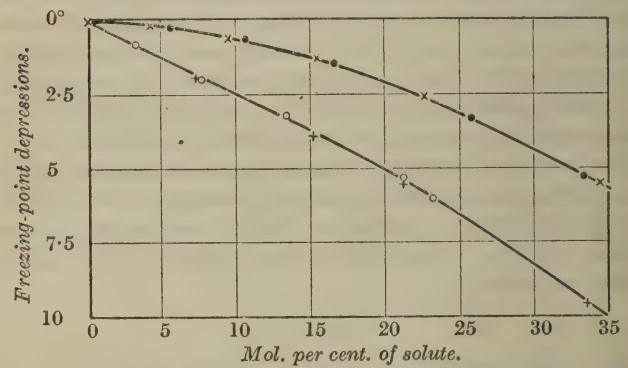
These results are expressed graphically in Fig. 1. Partial dis- ciation of the compound on fusion is shown by the fact that hyl acetate does not give the same freezing-point depression rve as the other solutes. By application of equation (II) above, is found that the approximate degree of dissociation of the com- und in the liquid state is 12%. The assumption of this value x gives practically perfect agreement throughout the whole gth of the experimental and calculated curves.

The value for Q, obtained calorimetrically for use in these calcul- ons, was 5170 ± 50 calories. This was checked by a rather ricate calculation from the freezing-point depression curve tained with benzene as solute. The value so derived was 50 ± 100 calories.

A most unexpected result in the above table is the identity of th freezing-point depression curves obtained with benzene (an ine solute) and water (presumably reactive). In this connexion it ma be mentioned that the points on the water curve did not chang significantly with time during the course of the determination hydrolysis effects evidently being quite slow at the low temperature involved. Comment upon the abnormal position of the water curv will be made at the conclusion of this article.

FIG. 1.

Freezing-point depression curve of the compound: ethyl acetate–trichloroacetic acid.



○ = Benzene. + = Water. × = Ethyl acetate (experimental). ● = Eth acetate (calculated for 12% dissociation of pure compound on fusion).

2. *The Compound Benzyl Benzoate–Trichloroacetic Acid.*—Th pure compound in this case melted sharply at 13·6°. The freezing point depression results obtained with benzyl benzoate, benzene, an water as solutes are given below.

TABLE II.

Freezing-point Depression Curves of the Compound: Benzyl Benzoate–Trichloroacetic Acid.

Solutes.						
Benzyl benzoate	Mol. %	4·54	9·92	15·75	26·1	51·7
	$\Delta T°$	0·10	0·35	0·80	2·0	8·5
Benzene	Mol. %	5·37	13·6	27·6	42·6	
	$\Delta T°$	1·40	3·6	8·1	14·4	
Water	Mol. %	7·58	10·87	19·7	27·0	
	$\Delta T°$	1·80	2·9	5·8	8·6	

Again the benzene and water curves are very nearly identica Calculation of the degree of dissociation of the compound on fusio from the position of the benzyl benzoate curve, using a calorimetri ally determined value for Q of 5660 $\pm$ 40 calories, leads to a valu of (approximately) 35%.

3. *The Compound Methyl Succinate–Trichloroacetic Acid.*—A pure ample of this compound (which contains one molecule of ester to wo of acid) melted sharply at 8·3°.

TABLE III.

Freezing-point Depression Curves of the Compound: Methyl Succinate–Trichloroacetic Acid.

Solutes.						
Methyl succinate	Mol. %	4·52	9·27	18·55	29·3	44·8
	$\Delta T°$	0·30	0·50	1·70	3·8	9·6
Benzene	Mol. %	5·55	11·97	21·8	31·3	
	$\Delta T°$	0·85	1·90	4·0	6·3	

The calculation of the degree of dissociation of this 1 : 2 compound rom the position of the methyl succinate curve is more complicated han in the previous cases. It is also more uncertain, since a com- ound of the type AB_2 may give an intermediate dissociation pro- uct AB as well as its simple components A and B. Fortunately, his particular compound is exceptionally stable, so that it is still ossible to fix its degree of dissociation between the upper and lower mits of 6 and 4% respectively. In this calculation, the value used or Q (9600 calories) is derived from the benzene curve, assuming this or the sake of simplicity to be ideal.

The Stability of Acid–Ester Compounds in Dilute Benzene Solution.

The next step in the investigation was to determine the stability f acid–ester compounds in the presence of a large excess of an nert solvent—benzene.

The compound ethyl acetate–trichloroacetic acid was first studied. able IV gives the freezing-point depression curves of benzene ith ester, acid and compound as solutes. The same data are epresented graphically in Fig. 2. For comparison, the ideal curve btained by substituting $Q = 2370$ calories and $T_0 = 278{\cdot}48$ n the equation $-\log_e(1-x) = Q/R \,.\, (1/T - 1/T_0)$, where = mol. % of solute] is also added.

TABLE IV.

Freezing-point Depression Curves of Benzene (System: Ethyl Acetate–Trichloroacetic Acid).

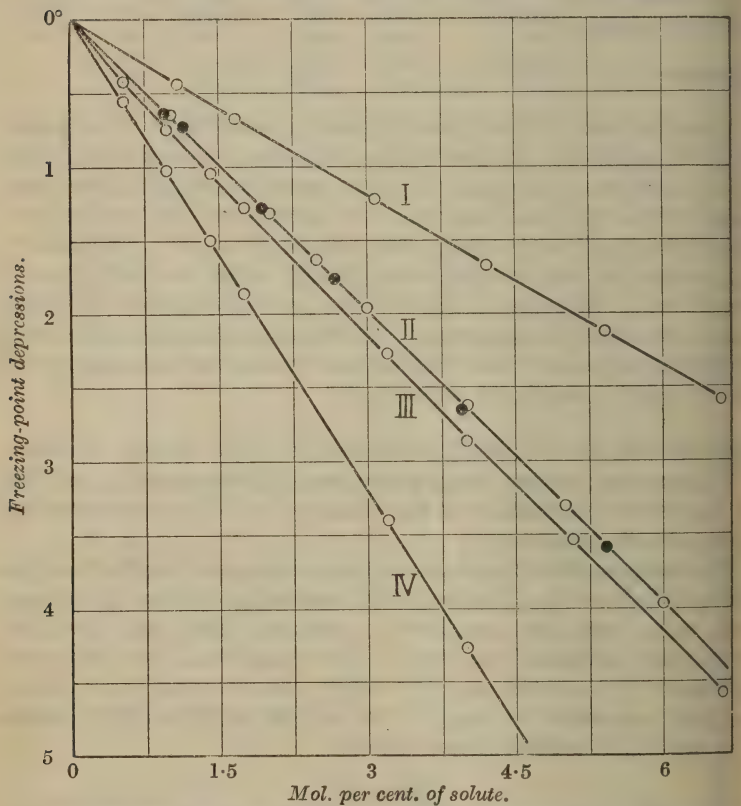
Solutes.								
Ideal	Mol. %	1·0	2·0	2·5	3·0	4·0	5·0	6·0
	$\Delta T°$	0·652	1·308	1·637	1·967	2·631	3·299	3·967
Ethyl acetate	Mol. %	0·965	1·138	1·934	2·670	3·966	5·425	
	$\Delta T°$	0·643	0·727	1·276	1·775	2·640	3·598	
Trichloro-	Mol. %	0·543	1·063	1·654	3·068	4·22	5·41	6·63
acetic acid	$\Delta T°$	0·213	0·432	0·672	1·222	1·674	2·120	2·582
Acid–ester	Mol. %	0·520	0·952	1·410	1·743	3·205	4·065	5·075	6·62
compound	$\Delta T°$	0·417	0·740	1·038	1·273	2·264	2·866	3·532	4·580

Specially purified benzene was employed in this work, and temperatures were read to 0·001° by the Beckmann method. The thermometer employed was calibrated by the Bureau of Standards and all precautions were taken to ensure accuracy.

The ethyl acetate curve, it will be seen from the diagram, follows

FIG. 2.

System: ethyl acetate–trichloroacetic acid. Benzene as solvent.



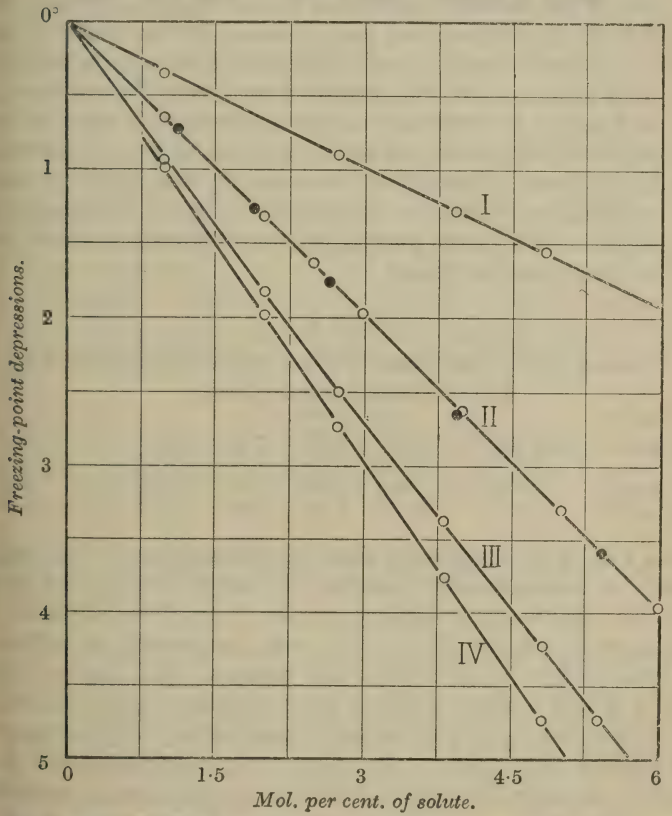
I *Trichloroacetic acid.* II *Ethyl acetate* (●); *ideal curve* (○). III *Additive compound.* IV *Sum of* I *and* II.

the ideal within error limits. The freezing-point depressions induced by trichloroacetic acid, however, are much less than normal. Examples of this type have been interpreted in the past as indicative of the fact that the solute is associated in the solution, but the conception of Hildebrand (*J. Amer. Chem. Soc.*, 1916, **38**, 1452) that a positive deviation from Raoult's law is consequent upon differences in the internal pressures of the two components of the solution

ffers an alternative explanation. This point will be discussed later. he curve given by the compound, if this were completely dissociated n the solution into ester and acid, would be the sum of the depressions iven by its components separately. This is shown as curve IV on ie diagram. (For strict purposes of comparison, it may be noted,

FIG. 3.

System: ethyl acetate–acetic acid. Benzene as solvent.



I *Acetic acid.* II *Ethyl acetate* (●); *ideal curve* (○). III *Ethyl acetate+ etic acid (experimental).* IV *Sum of* I *and* II.

ie deviation of the ideal freezing-point depression curve from nearity should be taken into account, and curve IV should fall ightly below the sum of curves I and II, but the error introduced y the simpler procedure here adopted is negligible throughout this ork.) The actual curve obtained, curve III, lies considerably ove curve IV, demonstrating that a large proportion of the mpound is still existent as such in the system in spite of its reduced

concentration. The exact degree of dissociation at any given dilution cannot, however, be determined, since we have no means of knowing whether the curve for the undissociated compound follows the ideal or not. Most probably it would lie intermediately between the curves given by its two components, and we may therefore infer that the bulk of the compound is still undissociated when its concentration is diminished to 1—6 mol. %.

In view of the indefinite character of the results obtainable, the work in benzene solution was not extended to the additive compounds of benzyl benzoate and methyl succinate with trichloroacetic acid discussed in the preceding sections. It did seem of sufficient interest, nevertheless, to determine whether the existence of an ester–acid compound, already so unstable in the liquid state as to inhibit its direct isolation from the binary system by the freezing-point method, could still be established in dilute solution in an inert solvent. The results for the system ethyl acetate–acetic acid are given below and in Fig. 3.

TABLE V.

Freezing-point Depression Curves of Benzene (System: Ethyl Acetate–Acetic Acid).

Solutes.							
Acetic acid	Mol. %	0·993	2·75	3·93	4·84		
	$\Delta T°$	0·343	0·905	1·284	1·559		
Acetic acid + ethyl acetate	Mol. %	1·000	2·016	2·751	3·834	4·82	5·38
	$\Delta T°$	0·938	1·827	2·503	3·372	4·215	4·835

From Fig. 3 it is apparent that the freezing-point depressions induced by equimolecular quantities of ethyl acetate and acetic acid taken together are slightly smaller than those obtained by summing up the effects of the two separate components, an indication that some additive compound is still present. The degree of dissociation of this compound at any given dilution is again uncertain, owing to the abnormality of the acetic acid curve, but it is evidently much greater than that of the ethyl acetate–trichloroacetic acid compound, as might be expected with a weak acid as one component.

The Internal Pressure Factor in Freezing-point Depression Curves.

It remains to discuss briefly the abnormalities noted in the various systems examined. These, it will be found, all occur in systems in which we have a polar solute and a non-polar solvent, and in all cases the observed freezing-point depression is less than anticipated. Now Hildebrand (*loc. cit.*) has shown that an abnormally small freezing-point depression is a general characteristic of such systems, in which the internal pressures of the two components

n the liquid state are markedly different. While, therefore, associ-tion of the solute may occur to a minor extent in the cases of richloroacetic acid and acetic acid in benzene, yet the abnormally mall freezing-point depressions obtained must be ascribed, in the nain, to the internal pressure factor.

The freezing-point depression curves of the ester–acid compounds vith water as solute may be explained in the same way. We should ertainly expect water to dissociate these compounds to a far greater legree than benzene, yet the two solutes give curves which are ractically coincident. The curves ought to be widely divergent, part from any question of instability of the solvent, since water nd benzene have internal pressures so very far apart from each ther that they cannot both be ideal solutes in the same liquid. Iost probably, therefore, very extensive dissociation of the ester–cid compound on addition of water does occur, but the negative eviation from Raoult's law consequent thereupon is obscured by a imultaneous positive deviation from Raoult's law due to the internal ressure factor. Confirmation for this view will be found in the esults of the succeeding article, in which the stability of ester–acid ompounds in dilute aqueous solution is examined in detail.

Summary.

The stability of three ester–acid additive compounds on fusion as been investigated. The approximate degrees of dissociation re :

(*a*) Ethyl acetate–trichloroacetic acid (m. p. −26·8°); 12%.
(*b*) Benzyl benzoate–trichloroacetic acid (m. p. 13·6°); 35%.
(*c*) Methyl succinate–trichloroacetic acid (m. p. 8·3°); 4—6%.

These values refer to different temperatures (an unavoidable efect of the freezing-point method employed), but the order of tability is in accordance with previous work. Changes in degree f dissociation with temperature are presumably small. The mole-ular heats of fusion of the three compounds are 5170, 5660, and 600 calories respectively.

In dilute benzene solution (at temperatures slightly above 0°) ie compound ethyl acetate–trichloroacetic acid is still markedly :able, and the decomposition of such a weak complex as ethyl cetate–acetic acid is not complete.

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CCXXXVI.—*Additive Compounds in the Ternary System: Ester–Acid–Water.*

By James Kendall and Cecil Victor King.

Several distinct lines of attack have been followed in this investigation, in the hope that the results obtained by converging upon the problem from different angles, together with the various suggestions derived from the simpler binary systems, might furnish greater opportunity for an advance. The freezing-point depression data which form the main part of the work are consequently discussed and correlated with conductivity and reaction velocity determinations at 0°. It is unfortunate that the extensive experimental data of previous investigators on certain of the systems studied cannot be employed to any considerable degree in this comparison, but the majority of such measurements refer to higher temperatures and are not readily reducible to molecular concentration units.

In this paper the four systems ethyl acetate–hydrochloric acid, ethyl acetate–trichloroacetic acid, ethyl acetate–chloroacetic acid and ethyl acetate–acetic acid are examined in detail, with the idea of ascertaining how conditions vary when a representative ester is paired against a series of acids of widely divergent strengths.

Binary Systems Acid–Water and Ester–Water.

Systems of the type acid–water have already been critically investigated by Kendall, Booge, and Andrews (*J. Amer. Chem. Soc.*, 1917, **39**, 2303), and the general law has been deduced that compound formation increases with the strength of the acid. Little work has been done upon systems of the type ester–water. Griffith and Lewis (J., 1916, **109**, 80) have postulated an additive ester-water compound as an intermediate step in ester hydrolysis, but the freezing-point depression data of Rivett for ethyl acetate (*Z. physikal. Chem.*, 1912, **80**, 547), when recalculated on a molecular concentration basis, follow the ideal curve almost exactly. On account of this fact the opinion was expressed (*J. Amer. Chem. Soc.*, 1916, **38**, 1716) that ester–water compounds could not be formed in more than minute quantity. Our own freezing-point depression determinations for ethyl acetate, presented in Table I below (see also Fig. 1), are in complete accordance with those of Rivett, yet a more intensive study of the system leads us now to reverse our judgment.

Briefly, ethyl acetate is a "pseudo-ideal" solute in water, two opposing factors practically counterbalancing each other. The fact that ethyl acetate and water are only partly miscible (due to

ternal pressure differences) precludes all possibility of a normal eezing-point depression curve; the experimental depressions ould be considerably less than the ideal (see Hildebrand, "Solulity," A. C. S. Monograph Series, 1924; also p. 1777 of the preding article). The only factor that could depress the curve ack again to correspond with the ideal is extensive compound rmation between ester and water, and there are several points hich indicate that extensive compound formation actually does cur. Liquids which are partially miscible normally give absorpon of heat on admixture, but heat is evolved, not absorbed, when hyl acetate is dissolved in water. The rapid increase in the lubility of the ester as the temperature is lowered suggests that compound is formed, the stability of which increases with falling mperature (Hildebrand, *loc. cit.*, p. 144). The fact that the ensity of the saturated solution at 0° is greater than unity (Seidell, Solubilities of Inorganic and Organic Compounds," D. van ostrand Co., 1919, p. 285) demonstrates that remarkable conaction accompanies admixture, and this contraction is most mply explained on the assumption of compound formation.

Other systems of the type R·CO·OR′–H_2O are now being examined discover how these two opposing factors—internal pressure fference and compound formation—vary with the nature of the dicals R and R′. For the present, it suffices to know that all ree possible binary systems (ester–acid, acid–water, and ester–ater) give additive compounds, and it becomes necessary to termine to what extent these survive in the ternary system and hether any ternary compounds are formed.

Freezing-point Depression Determinations.

The freezing-point depression results obtained with water on ldition of ethyl acetate, the four acids, and equimolecular quantities ester and each acid taken together, are presented in Table I. ne data for the hydrochloric and acetic acid systems are also ven in Figs. 1 and 2, respectively.

At first the measurements for solutions containing both acid nd ester were made at known time intervals after mixing, with e intention of extrapolating to zero time to correct for the change freezing point due to hydrolysis. This procedure was, however, und to be unnecessary, as the freezing point in the most conntrated solution of the strongest acid did not vary more than a w thousandths of a degree in a whole hour. The experimental ocedure was the same as that employed with benzene as solvent the preceding article. The values given below are the results duplicate measurements, checking to $\pm 0{\cdot}002°$.

TABLE I.

Freezing-point Depression Curves of Ester–Acid Solutions.

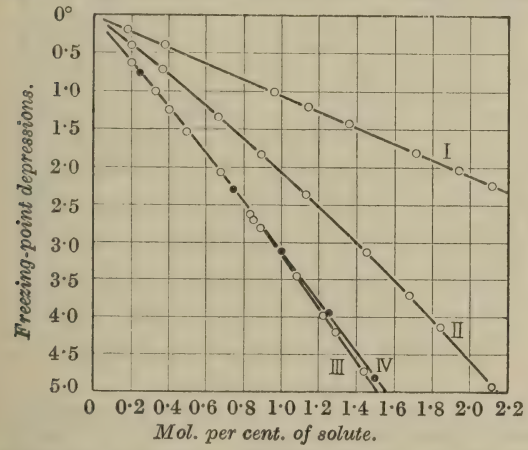
Solutes.							
Ethyl acetate	Mol. %	0·181	0·379	0·574	0·963	1·148	1·362
	$\Delta T°$ (obs.)	0·190	0·398	0·594	1·007	1·203	1·431
	$\Delta T°$ (ideal)	0·187	0·391	0·592	0·994	1·185	1·406
	Mol. %	1·718	1·945	2·134			
	$\Delta T°$ (obs.)	1·797	2·034	2·224			
	$\Delta T°$ (ideal)	1·773	2·007	2·202			
Hydrochloric acid	Mol. %	0·204	0·369	0·666	0·897	1·139	1·457
	$\Delta T°$	0·398	0·720	1·335	1·835	2·374	3·142
	Mol. %	1·686	1·851	2·136			
	$\Delta T°$	3·703	4·126	4·931			
Ethyl acetate + hydrochloric acid	Mol. %	0·209	0·335	0·409	0·499	0·681	0·838
	$\Delta T°$	0·626	1·008	1·247	1·525	2·099	2·637
	Mol. %	0·858	0·893	1·086	1·230	1·297	1·446
	$\Delta T°$	2·702	2·817	3·466	3·979	4·194	4·727
Trichloroacetic acid	Mol. %	0·277	0·528	0·765	1·002	1·264	1·439
	$\Delta T°$	0·530	0·994	1·451	1·884	2·373	2·697
	Mol. %	1·722	2·032	2·293	2·541		
	$\Delta T°$	3·223	3·791	4·256	4·697		
Ethyl acetate + trichloroacetic acid	Mol. %	0·176	0·259	0·409	0·554	0·728	0·856
	$\Delta T°$	0·510	0·748	1·187	1·592	2·063	2·434
	Mol. %	0·944	1·042				
	$\Delta T°$	2·651	2·869				
Chloroacetic acid	Mol. %	0·160	0·338	0·592	0·931	1·360	1·647
	$\Delta T°$	0·176	0·369	0·639	0·978	1·395	1·667
	Mol. %	1·755	1·999				
	$\Delta T°$	1·766	1·989				
Ethyl acetate + chloroacetic acid	Mol. %	0·249	0·473	0·593	0·904	1·256	1·314
	$\Delta T°$	0·525	0·988	1·227	1·826	2·448	2·548
	Mol. %	1·513	1·709	1·791			
	$\Delta T°$	2·866	3·153	3·264			
Acetic acid	Mol. %	0·537	0·902	1·341	1·624	1·871	2·393
	$\Delta T°$	0·556	0·952	1·381	1·663	1·916	2·442
	Mol. %	2·896					
	$\Delta T°$	2·944					
Ethyl acetate + acetic acid	Mol. %	0·176	0·303	0·437	0·819	0·957	1·161
	$\Delta T°$	0·373	0·634	0·917	1·667	1·941	2·353
	Mol. %	1·523	1·674	2·035	2·217	2·631	
	$\Delta T°$	3·042	3·315	3·919	4·202	4·775	

The significance of the data may be most readily appreciate by reference to the diagrams. In the hydrochloric acid syste (Fig. 1), the freezing-point depressions induced by acid and este taken together (curve III) are almost identical with the sum o the depressions induced by corresponding concentrations of th two separately (curve IV). Now if the ester–acid comple R·CO·OR′,HX were completely stable in solution, we shoul expect its curve to follow approximately the ethyl acetate (c ideal) curve (I) in the event of its being a non-electrolyte, or th hydrochloric acid curve (II) in the more probable event of it being a strong electrolyte giving the ions $[R·CO·OR',H]^+$ and X^-

n intermediate position between (I) and (II), or between (II) d (IV), would follow from partial dissociation. The actual sition of the curve indicates, however, complete dissociation the compound into its components, and also demonstrates that rnary complexes cannot exist in any significant quantity in the lution. (In point of fact, curve III lies very slightly below rve IV. This discrepancy may be explained, however, by king into account the slight deviation of the ideal curve from earity [compare p. 1775], accentuated in this case by hydration the solutes.) To explain the total instability of the ester–acid mpound in water solution we need only to consider that the

FIG. 1.

System : ethyl acetate–hydrochloric acid. Water as solvent.



I *Ethyl acetate* (*also ideal curve*). II *Hydrochloric acid.* III *Ethyl acetate* + *rochloric acid* (*experimental*, ○). IV *Sum of* I *and* II (●).

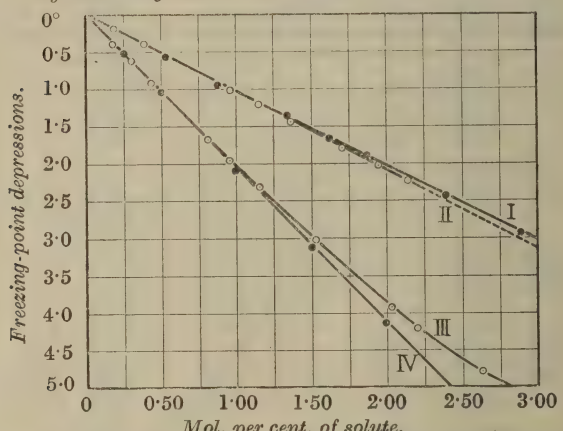
er and the water function as rival bases, competing for the session of the hydrochloric acid. Alone, each is able to furnish able additive compound (or oxonium salt); but in dilute aqueous ition the enormous excess of water and its more highly basic racter lead to essentially complete destruction of the ester–acid plex.

n the acetic acid system (Fig. 2), on the other hand, the freezing- nt depressions obtained with acid and ester together are, at higher concentrations examined, appreciably less than the n of those obtained with the two solutes separately. The same ults are given by the trichloroacetic and chloroacetic acid systems, difference at equivalent concentrations (*e.g.*, 1 mol. %) increasing h the strength of the acid. This might be argued to indicate

that a small fraction of the ester–acid complex does, after al escape decomposition, the fraction increasing with the strengt of the acid. On this basis, the results for the hydrochloric aci system alone would have to be regarded as abnormal. Alter atively, the three freezing-point depression curves in a syste containing an organic acid may be considered as not strictly con parable, owing to differences in internal pressure and associatio factors. It is significant, in this connexion, that chloroacetic an acetic acids already give small positive deviations from Raoult law in concentrated aqueous solution, before any addition of este

FIG. 2.

System : ethyl acetate–acetic acid. Water as solvent.



I *Acetic acid.* II *Ethyl acetate (prolonged as ideal curve beyond saturatio* III *Ethyl acetate + acetic acid (experimental).* IV *Sum of* I *and* II.

Before this question is discussed further, the conductivity a velocity of reaction results for equimolecular mixtures of eth acetate with the four acids will be presented. A final feature the freezing-point depression curves may be noted here: t maximum concentration that can be investigated varies ve remarkably in the four systems. It is not possible, of course, carry out exact solubility measurements under the conditions experiment, but the approximate molecular concentrations which two liquid layers first persist, when equivalent quantiti of ethyl acetate and acid are added to water at 0°, are as follow

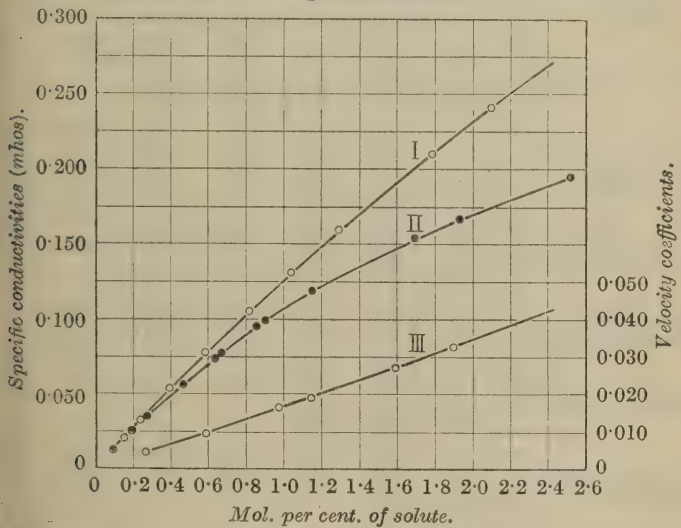
Ester alone.	Ester + HCl.	Ester + $CCl_3 \cdot CO_2H$.	Ester + $CH_2Cl \cdot CO_2H$.	Ester + $CH_3 \cdot CO_2H$.
2·2	2·55	1·1	1·75	2·75

It would be hazardous to offer even a tentative explanation these solubility changes. If the second phase were fixed (as

he case of a solid solute), an increase in solubility could be interreted as indicative of compound formation. In the present nstance, however, the saturating phase is not pure ethyl acetate, ut a second liquid layer containing dissolved water and acid, so hat no general comparison can be made. The run of the figures certainly very curious, the strongest and weakest acids causing ncreased solubility and the intermediate acids decreased solubility. The 50% decrease of solubility in the presence of trichloroacetic cid, a substance perfectly miscible with both ester and water, is articularly mystifying.

FIG. 3.

System: ethyl acetate–hydrochloric acid. Specific conductivities and reaction velocities in aqueous solution at 0°.



I *Hydrochloric acid.* II *Hydrochloric acid + ethyl acetate.* III *Reaction elocities: equimolecular ester–acid solutions.*

Specific Conductivity Determinations.

A General Radio Co. audio-oscillator, giving a nearly pure sine-ave alternating current at a frequency of 1000 per second, was sed as the source of current. With solutions of high resistance a harper minimum was obtained by inserting a two-stage thermionic mplifier (compare Hall and Adams, *J. Amer. Chem. Soc.*, 1919, 4, 1515). The bridge was a Leeds and Northrup 4·7 metre circular side-wire instrument, with resistance coils from 0·1 to 10,000 ohms. Ildwin type G telephones were employed.

The conductivity cells were of the Washburn dumb-bell type, with unplatinised electrodes. Their constants, 128·66 and 0·3694

respectively, were determined according to the directions of Kra and Parker (*J. Amer. Chem. Soc.*, 1922, **44**, 2422). Small variab air condensers were used across the resistances to balance out th cell capacity. All measurements were made in a large bath cracked ice and water, the temperature of which was constan at $-0{\cdot}02 \pm 0{\cdot}005°$. Conductivities taken at known time interva after mixing the acid–ester solutions showed that in no case wa it necessary to extrapolate back to zero time, hydrolysis at being sufficiently slow to exercise no significant effect during th time of measurement.

TABLE II.

Specific Conductivities of Ester–Acid Solutions at 0°.

Solutes.							
Hydrochloric acid	Mol. %	0·157	0·242	0·396	0·588	0·817	1·056
	$\kappa \times 10^2$	2·158	3·294	5·283	7·693	10·47	13·23
	Mol. %	1·298	1·799	2·105	2·753		
	$\kappa \times 10^2$	15·93	21·12	24·05	29·68		
Hydrochloric acid + ethyl acetate	Mol. %	0·099	0·199	0·271	0·461	0·637	0·644
	$\kappa \times 10^2$	1·321	2·633	3·503	5·646	7·468	7·525
	Mol. %	0·857	0·899	1·155	1·699	1·923	2·521
	$\kappa \times 10^2$	9·490	9·860	11·81	15·29	16·69	19·44
Trichloroacetic acid	Mol. %	0·212	0·270	0·475	0·524	0·738	0·907
	$\kappa \times 10^2$	2·473	3·082	5·027	5·489	7·235	8·448
	Mol. %	1·507					
	$\kappa \times 10^2$	11·77					
Trichloroacetic acid + ethyl acetate	Mol. %	0·208	0·414	0·553	0·751	1·104	
	$\kappa \times 10^2$	2·357	4·196	5·214	6·414	7·914	
Chloroacetic acid	Mol. %	0·160	0·338	0·592	0·931	1·360	1·647
	$\kappa \times 10^3$	2·909	4·354	5·793	7·180	8·441	9·080
	Mol. %	1·755	1·999				
	$\kappa \times 10^3$	9·290	9·707				
Chloroacetic acid + ethyl acetate	Mol. %	0·228	0·422	0·563	0·883	1·165	1·393
	$\kappa \times 10^3$	3·357	4·414	4·922	5·652	6·004	6·129
	Mol. %	1·727					
	$\kappa \times 10^3$	6·175					
Acetic acid	Mol. %	0·205	0·390	0·619	0·817	1·071	1·174
	$\kappa \times 10^4$	3·420	4·644	5·765	6·474	7·264	7·519
	Mol. %	1·397	1·744	2·126	2·911		
	$\kappa \times 10^4$	8·063	8·731	9·279	10·11		
Acetic acid + ethyl acetate	Mol. %	0·169	0·306	0·557	0·861	1·112	1·412
	$\kappa \times 10^4$	2·962	3·736	4·720	5·315	5·563	5·699
	Mol. %	1·795	2·181	2·366	2·723		
	$\kappa \times 10^4$	5·698	5·589	5·506	5·306		

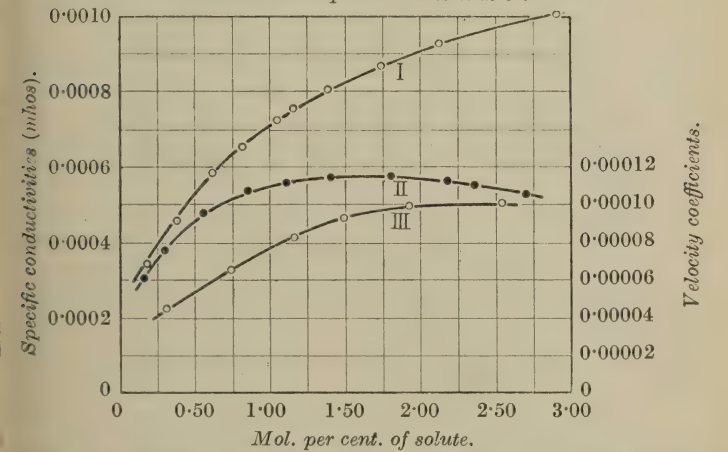
The curves for the hydrochloric and acetic acid systems ar shown in Figs. 3 and 4. It will be seen that the addition of a equivalent quantity of ethyl acetate brings about a considerab diminution in the specific conductivity of the acid solutions, th effect being more pronounced the higher the concentration. I the acetic acid system, the reduction is actually sufficient to cau a decrease in the specific conductivity at concentrations abo

·6 mols. %. The percentage reduction increases as the acidic trength decreases, the lowering of specific conductivity for the our systems at 1·0 mol. % being : HCl, 16% ; $CCl_3{\cdot}CO_2H$, 18% ; $H_2Cl{\cdot}CO_2H$, 23% ; $CH_3{\cdot}CO_2H$, 24%. (The increase in the volume f the solution due to the addition of ester at this concentration, may be noted, is less than 5%. The reduction in specific con- uctivity, therefore, is not simply due to dilution.)

This phenomenon has been noted previously by Griffith and ewis (*loc. cit.*). The most obvious means of accounting for the bserved decrease is to assume compound formation of ester with cid in the solution. If the ester–acid complex R·CO·OR′,HX

FIG. 4.

System : ethyl acetate–acetic acid. Specific conductivities and reaction velocities in aqueous solution at 0°.



I *Acetic acid, alone.* II *Acetic acid + ethyl acetate.* III *Reaction velocities : uimolecular acid–ester solutions.*

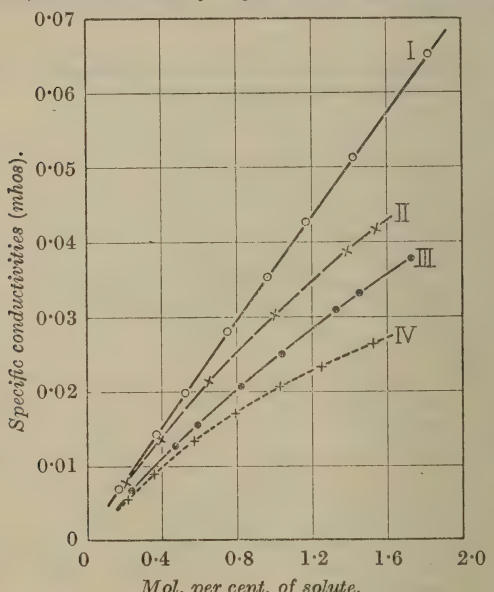
mained non-ionised, then its formation would lower the con- ntrations of both H^+ and X^-, whilst if it were an electrolyte the ain factor would be the replacement of the rapidly-moving ion H^+ the less mobile complex $[R{\cdot}CO{\cdot}OR',H]^+$. Two alternative planations, however, must also be considered : (*a*) the addition ester may cause a decrease in the dielectric constant of the lution and so reduce the extent of ionisation of the acid, or (*b*) the ldition of ester may simply decrease the mobility of the ions thout changing their nature (compare alcohol–water mixtures, dlewski, *Z. physikal. Chem.*, 1905, **51**, 751).

None of these three explanations is in entire harmony with the ezing-point depression results already recorded for the same stems. The extent of compound formation demanded by the

first is much greater than that indicated by the freezing-poi curves for the three organic acids, while the hydrochloric acid da are in direct conflict with any assumption of ester–acid comple survival in the system. Under the second explanation, not onl are the observed freezing-point depression curves abnormal i the case of the two strong acids, but it is necessary to assume a enormous decrease in the dielectric constant for the addition of small amount of ester. The following experiments may be regarde

FIG. 5.

Specific conductivities of ethyl acetate–salt solutions at 0°.



I *Potassium chloride, alone.* II *Potassium chloride + ethyl acetat* III *Potassium acetate, alone.* IV *Potassium acetate + ethyl acetate.*

as definitely eliminating these two hypotheses, and thereby increasi the likelihood that the third is, in general, valid.

The effect of addition of ester on the specific conductivities neutral salt solutions may first be considered. Potassium chlori and potassium acetate were selected as typical derivatives of strong and a weak acid respectively, and the determinations, carri out exactly as in the case of the acid solutions, are summarised Table III and Fig. 5.

It is evident from Fig. 5 that the addition of ester decreases t specific conductivity of a neutral salt solution just as effective as it does that of an acid solution. At a concentration of 1·0 mol.

TABLE III.

Specific Conductivities of Ester–Salt Solutions at 0°.

Solutes.							
otassium chloride	Mol. %	0·167	0·372	0·523	0·755	0·965	1·172
	$\kappa \times 10^2$	0·688	1·424	1·969	2·798	3·535	4·259
	Mol. %	1·424	1·820				
	$\kappa \times 10^2$	5·132	6·521				
otassium chloride	Mol. %	0·204	0·390	0·645	1·000	1·396	1·540
- ethyl acetate	$\kappa \times 10^2$	0·780	1·388	2·131	3·027	3·892	4·183
otassium acetate	Mol. %	0·245	0·479	0·597	0·829	1·046	1·345
	$\kappa \times 10^2$	0·688	1·270	1·547	2·063	2·507	3·091
	Mol. %	1·458	1·735				
	$\kappa \times 10^2$	3·298	3·775				
otassium acetate	Mol. %	0·215	0·360	0·575	0·797	1·039	1·256
- ethyl acetate	$\kappa \times 10^2$	0·587	0·919	1·344	1·717	2·063	2·333
	Mol. %	1·532					
	$\kappa \times 10^2$	2·628					

ıe decrease for potassium chloride is 17%, and for potassium :etate 18%. Now there is certainly no compound formation :twee the ester and the neutral salts in the solution to the extent dicated by these figures. We must consequently conclude that .e decrease in specific conductivity induced by the presence of .e ester is due to some general effect, quite unconnected with the rmation of specific additive compounds.

A choice between the second and the third hypothesis is possible rough hydrogen-ion concentration measurements. If the decrease specific conductivity is due to a lowering of the dielectric con-ınt, the hydrogen-ion concentration of the solution should diminish ıen ester is added, whereas a mere diminution in ionic mobilities ould leave the hydrogen-ion concentration unchanged. Un-:tunately, attempts to obtain direct hydrogen-ion concentration terminations by the hydrogen electrode method gave inconclusive ;ults, since it was found that the potential of the hydrogen-ion :ctrode in a freshly prepared acid–ester solution at 0° was practic-y the same as in the same solution after hydrolysis had run to mpletion, or as in a solution containing equivalent quantities the hydrolysis products, acetic acid and ethyl alcohol. Appar-tly the hydrolysis is catalysed so rapidly by the platinum black ıt in the immediate vicinity of the electrode equilibrium con-ions are reached almost instantaneously. This point is being ıdied further, with modifications of method.

The matter may be decided indirectly, however, by determining) effect of the addition of ethyl acetate on the rate of sucrose ersion in an acid solution. Previous experiments by Coppadoro (*Gazzetta*, 1901, **31**, i, 425) with methyl acetate suggested that a ısiderable reduction does occur, but Henri and des Bancels

(*Compt. rend. Soc. Biol.*, 1901, **53**, 784) and Griffith and Lew (*loc. cit.*) agree that the same ester exercises practically no influenc With ethyl acetate the following results at 0° were obtained :

Mol. % of solutes.	Inversion constan
I. Sucrose 1·5; HCl 1·5	0·01045
II. Sucrose 1·5; HCl 1·5; ethyl acetate 1·5	0·01035

The inversion was followed in a Schmidt and Haensch polar meter, reading to 0·01°. The solutions were placed in a 220 mm tube, immersed in a bath kept at 0 ± 0·01° and fitted as describe by Nelson and Beegle (*J. Amer. Chem. Soc.*, 1919, **41**, 559). Th inversion constants given above have an accuracy of ± 1%, s it is clear that addition of ester induces practically no change i the rate of inversion and presumably, therefore, no significa change in the hydrogen-ion concentration of the solution. Dimi ution of ionic mobility is consequently to be regarded as the probab cause of the lowering in specific conductivity recorded in Tables I and III.

Determinations of Velocity of Hydrolysis.

The rates of hydrolysis of ethyl acetate at 0° in the presenc of equivalent quantities of the four acids up to the saturatio concentration are given in Table IV below. The curves for th hydrochloric and acetic acid systems are shown also in Figs. and 4. The course of the hydrolysis was followed by the usu method of withdrawing samples from the bath at intervals an titrating against potassium hydroxide, standardised against hydr chloric acid and free from carbonate. The time required fo solutions of the weaker acid to reach equilibrium varied fro 1 to 8 weeks. In a few instances, it was necessary to determin the end value by raising the temperature to 25° for a time an then returning to 0° for a week or so to obtain a final adjustmen In view of the very small change with temperature of the positio of the equilibrium point in ester hydrolysis, no significant erro could be introduced by this hastening of the reaction.

The variation in the rate of hydrolysis, k, for the three strong acids approximated 1% in a single run. Duplicate runs agree also within this limit. For the acetic acid solutions, where hydr lysis proceeded extremely slowly, the variation was as much a 2—3%.

For simplicity, the reaction is treated here as if it were of simple unimolecular type, and all the constants are calculate on that basis. Griffith and Lewis (J., 1908, **109**, 67) have show it is true, that the hydrolysis must finally be regarded as bimol cular and reversible, but space does not permit us to discuss i

tail here the complete analysis of our data according to their uations. This matter will be taken up in full in a later paper; will suffice to state at this stage that the general conclusions veloped below are substantially unchanged under the more rigid ethod of calculation.

TABLE IV.

Reaction Velocities in Ester–Acid Solutions at 0°.

Solutes.							
hyl acetate + drochloric acid	Mol. %	0·271	0·598	0·970	1·151	1·597	1·909
	$k \times 10^2$	0·440	0·966	1·62	1·91	2·74	3·26
hyl acetate + chloroacetic acid	Mol. %	0·293	0·615	0·816	0·922	1·089	
	$k \times 10^2$	0·440	0·902	1·15	1·29	1·45	
hyl acetate + loroacetic acid	Mol. %	0·294	0·670	0·923	1·240	1·412	1·677
	$k \times 10^3$	0·484	0·754	0·855	0·952	0·984	1·04
hyl acetate + etic acid	Mol. %	0·316	0·742	1·170	1·496	1·926	2·541
	$k \times 10^4$	0·444	0·644	0·829	0·934	0·987	1·015

From the velocity coefficient curves for the hydrochloric acid stem in Fig. 3 it will be seen that the rate of hydrolysis increases uch more rapidly than the specific conductivity, and more rapidly deed than the molecular concentration of the acid. This may interpreted in two ways. First of all, it may be regarded as dicative of the fact, already noted in the freezing-point depression rve, that the "activity" of the hydrogen ion increases more pidly than the acid concentration, even when this is expressed molecular units. Alternatively, it may be construed, according the theory that the non-solvated hydrogen ion alone is catalytic- y active (recently revived by Rice, *J. Amer. Chem. Soc.*, 1923, , 2808), as signifying that the non-hydrated fraction of the drogen ion increases steadily as the concentration of the two utes is increased, owing to the diminishing concentration of e water present in the solution. The two statements are not ıtually exclusive, in all probability, but merely different methods expressing the same situation.

The curve for the acetic acid system (Fig. 4), on the contrary, ows a velocity coefficient increasing less rapidly than the specific nductivity of the acid in the absence of ester, although more pidly than the specific conductivity of the acid in the presence ester. A maximum reaction velocity is obtained at about · mols. %. Just as in the case of the freezing-point depression ta, the curves for the trichloroacetic acid and chloroacetic acid stems are similar in character to that for acetic acid, although ir rate of change of slope becomes less and less rapid as the ength of the acid is increased.

Further discussion of the rate of reaction curves would not be

profitable at this point, inasmuch as no quantitative comparison can be made between them and the specific conductivity curves until density and viscosity data for the solutions are available. These data will also render it possible to transpose the measurements here recorded to volume concentration units, and to utilise the results of previous workers. Whilst the conclusions drawn from this investigation are only preliminary and qualitative, yet the use of molecular concentration ratios has enabled several important deductions to be made. The main points of the work may be summarised briefly as follows:

Summary.

(1) Ethyl acetate gives a "pseudo-ideal" freezing-point depression curve in aqueous solution, and must consequently be extensively hydrated.

(2) The freezing-point depression caused by equivalent quantities of ethyl acetate and hydrochloric acid taken together is greater than the sum of the depressions due to the two separately. It follows that ternary complexes and ester–acid additive compounds are not existent in significant quantity in the aqueous solution. This conclusion is supported by specific conductivity data.

(3) Although the freezing-point depression curves obtained for trichloroacetic, chloroacetic, and acetic acids with ethyl acetate appear to indicate the survival of some ester–acid complex, yet the specific conductivity results in these systems also demonstrate decisively that no appreciable fraction actually persists. The freezing-point curves with these organic acids are presumably not strictly comparable, owing to internal pressure and association changes.

(4) The specific conductivity of a neutral salt, as well as of an acid, in aqueous solution is lowered by the addition of ethyl acetate. This lowering is due to diminished ionic mobilities.

(5) The rate of hydrolysis of ethyl acetate in the presence of hydrochloric acid in equivalent quantity increases more rapidly than the molecular concentration of the acid. With weaker acids the rate of hydrolysis increases less rapidly. In fact, the curve for acetic acid shows a maximum rate near the saturation point.

(6) The solubility of ethyl acetate in water at 0° varies very remarkably when electrolytes are also present in equivalent quantity.

(7) The rate of inversion of sucrose in hydrochloric acid solution at 0° is not affected by the addition of ethyl acetate. Inasmuch as the rate of ester hydrolysis is greatly increased by the addition of sucrose, it is clear that the mechanisms of the two reactions must be fundamentally different.

In conclusion it must be emphasised that, although it has been demonstrated that ester–acid additive compounds and ternary complexes of these with water do not exist in quantity in aqueous solution, yet this cannot be considered as proof that such compounds do not constitute intermediate steps in the reaction. An infinitesimal quantity of a compound at any one time would suffice for this purpose, its very instability serving, indeed, as a potent factor in the catalysis. The minimal extent to which these ester–acid compounds survive precludes further study of them by the freezing-point depression method, but valuable results are promised from a more intensive study of compounds of the type ester–water. The factors influencing the stability of compounds of this general type $R{\cdot}CO_2R',H_2O$ in the presence of an acid HX as R, R′, and X are varied, will be discussed in a forthcoming paper.

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CCXXXVII.—*The Preparation of Phthalamic Acids and their Conversion into Anthranilic Acids.*

By ERNEST CHAPMAN and HENRY STEPHEN.

PHTHALAMIC acid results from two additive reactions: (*a*) from water and phthalimide (Aschan, *Ber.*, 1886, **19**, 1403), and (*b*) from ammonia and phthalic anhydride (Auger, *Bull. Soc. chim.*, 1888, **9**, 349).

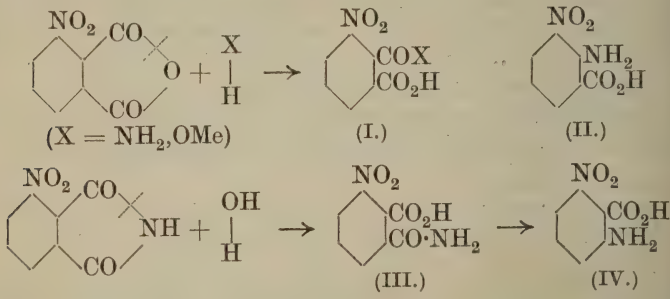
The modification and extension of Auger's method now described show that reaction (*b*) affords phthalamic acids in excellent yield. Since these acids react smoothly with sodium hypochlorite, anthranilic acids become readily accessible. Anthranilic acid and 3 : 5-dibromoanthranilic acid are readily obtained from the corresponding anhydrides.*

Unsymmetrical phthalic anhydrides, according to reaction (*b*), may give rise to one or both of two isomeric phthalamic acids, and it is of interest to discover (1) which amic acid is produced, alone or in the greater quantity, and (2) whether this amic acid is the same as that formed as chief product from the corresponding imide according to (*a*). The behaviour of 3- and 4-nitrophthalic anhydrides has been investigated from this point of view.

3-Nitrophthalic anhydride yielded exclusively 3-nitrophthalamic acid (I) (X = NH_2), which gave, in 90% yield, the 3-nitroanthranilic acid (II) obtained in small yield by Hübner by treatment of

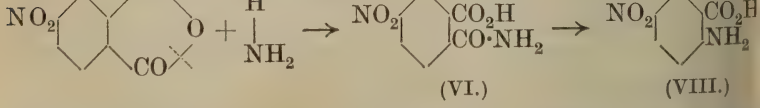
* The carboxyl group of phthalamic and anthranilic acids is numbered 1 and the amide or amine group 2.

" β-nitrosalicylic ester " with ammonia (*Annalen*, 1879, **195**, 37). Since 3-nitrophthalimide is converted by Hofmann's method almost entirely into 6-nitroanthranilic acid (IV) (Seidel, *Ber.*, 1901, **34**, 4352; Seidel and Bittner, *Monatsh.*, 1902, **23**, 415; Kahn, *Ber.*, 1902, **35**, 472), its preliminary hydrolysis must yield 6-nitrophthalamic acid (III).* The addition of methyl alcohol to 3-nitrophthalic anhydride is similar to that of ammonia (compare Wegscheider and Lipschitz, *Monatsh.*, 1900, **21**, 796).

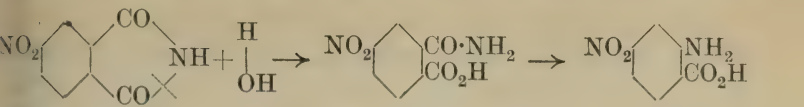


A comparison of these reactions shows that the negative component of the added molecule attaches itself to the carbonyl in the ortho-position to the nitro-group, and fission in all cases takes place at the same bond.

4-Nitrophthalic anhydride treated according to (*b*) gave an inseparable mixture of 4- and 5-nitrophthalamic acids (V and VI). The orientation and relative amounts of these acids were determined by conversion into the 4- and 5-nitroanthranilic acids (VII and VIII). These were obtained in the proportion of 2 to 3, whereas 4-nitrophthalimide gave the same mixture of acids but in the proportion of 4 to 1 (Seidel and Bittner, *loc. cit.*). This case is therefore parallel with that of the 3-nitro-compounds above, since the amic acid produced in greater yield by (*b*) is obtained in smaller yield by (*a*) and *vice versa*. The modes of addition which predominate in each reaction are as follows :



* Bogert and Boroschek (*J. Amer. Chem. Soc.*, 1901, **23**, 740) prepared this acid by the action of baryta on 3-nitrophthalimide, but wrongly described it as 3-nitrophthalamic acid. Kahn (*ibid.*, p. 3866) proved conclusively that it was 6-nitrophthalamic acid identical with the acid obtained by the action of ammonia on " 3-nitrophthal-β-methyl ester."



(V.) (VII.)

Here the negative components of the added molecules become ttached to the carbonyl in the *para*-position relatively to the nitro-roup.

In each of the cases considered, the course of the reactions cor-esponds with that observed with camphoric anhydride and camphor-mide, the former with ammonia (reaction *b*) giving α-camphoramic cid, whilst the latter on alkaline hydrolysis (reaction *a*) gives -camphoramic acid (see Lapworth, "On the Constitution of amphor," *Brit. Assoc. Reports*, Section B, 1900, p. 6).

Experimental.

Phthalamic Acid.—Phthalic anhydride (60 g.), added gradually ith stirring to warm aqueous ammonia (90 c.c.; d 0·88), dissolved eadily with considerable evolution of heat, and *ammonium phthal-mate* separated in fine, white crystals, the amount increasing on ooling (yield 70 g.; 94%) (Found: NH_3, 18·7. $C_8H_{10}O_3N_2$ requires NH_3, 18·4%). The salt was readily soluble in water, and was con-erted into phthalimide at about 200° without fusion. Phthalamic cid was obtained by treating the ammonium salt (30 g.) in cold ater (30 c.c.) with a slight excess of the equivalent quantity of oncentrated hydrochloric acid (20 c.c.) and washing the crystal-ne paste produced with cold water until it was free from hloride (yield 22 g.; 81%). The acid melted at 149° with loss of ater, solidified at 155°, and remelted at 231° (phthalimide). schan (*loc. cit.*) and Auger (*loc. cit.*) give m. p. 149° and 140° espectively. Aqueous solutions of the acid are more stable at the rdinary temperature than would be expected from Aschan's tatements.

Anthranilic Acid from Phthalamic Acid.—The "standard sodium ypochlorite solution" employed in this and all other cases to be escribed contained 47 g. of sodium hypochlorite and 50 g. of sodium ydroxide per litre.

Well-powdered phthalamic acid (20 g.) was gradually added to he stirred, cooled standard hypochlorite solution (200 c.c.), which ecame dark reddish-brown. Sodium hydroxide (10 g.) dissolved n water (50 c.c.) was now added, the mixture warmed at 80° for few minutes, cooled, and acidified with acetic acid. The anthr-nilic acid isolated by means of copper acetate and liberated from he copper salt with hydrogen sulphide melted at 145°.

4 : 5-*Dibromophthalamic Acid.*—4 : 5-Dibromophthalic anhydride prepared by boiling the corresponding acid with acetic anhydrid for several hours, separated from the filtered solution on cooli in fine, buff-coloured needles, m. p. 204—208°. Blümbein (*Be* 1884, **17**, 2490) gives m. p. 208°, Lesser and Weiss (*Ber.*, 191 **46**, 3937) give 214—215°. *Ammonium* 4 : 5-*dibromophthalama* was obtained in pale brown crystals (15·5 g.; 91%) by treating th anhydride (15 g.) with concentrated aqueous ammonia (22 c.c. On heating, it partly melted at 227° with loss of water and ammoni resolidified a few degrees higher, and remelted at 238—242° (th m. p. of 4 : 5-dibromophthalimide is given as 242—245° by Bruc *Ber.*, 1901, **34**, 2741, and as 245—246° by Lesser and Weiss, *loc. cit* see also below). 4 : 5-*Dibromophthalamic acid* was obtained fro the ammonium salt by addition of acid (yield 93%) (Found : B 49·6. $C_8H_5O_3NBr_2$ requires Br, 49·5%). It softened with loss water at 215—216°, being converted into the imide. Its aqueo solution reacted acid to litmus.

4 : 5-*Dibromophthalimide* was obtained in glistening yello needles, m. p. 242—243° (Found : Br, 52·85. Calc., Br, 52·4% by fusing the above amic acid and crystallising the product fro alcohol.

4 : 5-*Dibromoanthranilic Acid.*—Dibromophthalamic acid (10 g 1 mol.) was added as before to standard hypochlorite solutio (50 c.c.), and the yellow solution, after addition of sodium hydroxid (3 g.; 2 mols.) in water (20 c.c.), warmed to 80°, the colour becomin deep red. The 4 : 5-dibromoanthranilic acid precipitated from th solution, when cold, by a slight excess of hydrochloric acid crysta lised from dilute alcohol as a pale brown powder, m. p. 224° (decomp (8·5 g.; 94%) (Found : Br, 54·4. Calc., Br, 54·2%). Lesser an Weiss (*loc. cit.*) give m. p. 228—229°. The acid is almost insolubl in cold water, slightly soluble in hot water, and dissolves in th usual organic solvents except benzene, chloroform, and ligroin.

Treatment of the acid with acetic anhydride gave 4 : 5-*dibromo-2 acetylaminobenzoic acid*, fine, buff-coloured needles from dilut alcohol, m. p. 240° (Found : Br, 47·3. $C_9H_7O_3NBr_2$ require Br, 47·4%). Lesser and Weiss (*loc. cit.*, p. 3944) state that the obtained the acetyl derivative of the anhydride of the acid, m. p 184—185°.

* Anhydrides of dibasic acids are conveniently and rapidly prepared i almost quantitative yield as follows. The finely powdered, dry sodiu hydrogen salt (1 mol.) is warmed with thionyl chloride (3 mols.) for ½ hou and the excess of thionyl chloride removed by distillation. The residue anhydride and sodium chloride is boiled with benzene, and the solution filtered the pure anhydride crystallising from the filtrate.—H. S.

3- *and* 4-*Nitrophthalic Anhydrides*.—The corresponding acids re obtained by nitrating phthalic anhydride by Lawrence's thod (*J. Amer. Chem. Soc.*, 1920, **42**, 1872). An attempt to nvert the 4-nitro-acid into its anhydride by heating at 165—168° 3 hours as described by Lawrence (*loc. cit.*) proved unsatisfactory, product containing much unchanged acid. Both anhydrides re finally obtained by fusing the acids and then reducing the ssure to 22 mm. The temperature (thermometer in the liquid), 0—230° for the 3-nitro-acid and 170—180° for the 4-nitro-acid, s maintained for 1 hour. The brown melts crystallised on oling, and after recrystallisation from acetic anhydride or acetyl loride, 3-nitro- and 4-nitro-phthalic anhydrides were obtained ich melted at 163—164° and 115°, respectively, as stated by wrence.

3-*Nitrophthalamic Acid*.—The ammonium salt and the acid were tained from the anhydride (30 g.) and concentrated aqueous monia (45 c.c.) by the methods previously described (yield 87%). e *ammonium* salt consisted of fine, white needles, m. p. 172° comp.), giving 3-nitrophthalimide, m. p. 217—218° (Bogert and roschek, *loc. cit.*, m. p. 215—216°; Kahn, *Ber.*, 1902, **35**, 471, p. 216°). 3-*Nitrophthalamic acid* softens with loss of water at 3—174°, being converted into the imide. It is sparingly soluble cold and readily in hot water.

3-*Nitroanthranilic Acid*.—Finely powdered 3-nitrophthalamic d (10 g.; 1 mol.) was treated with 75 c.c. of standard hypochlorite ution (1 mol. NaOCl) in the usual way, and sodium hydroxide g.; 2 mols.), dissolved in water (10 c.c.), was added to the yellow ution. When the mixture was warmed at 80°, its colour gradually ame brick-red and a bright red precipitate of sodium 3-nitro- hranilate separated. Sufficient water was added to the cooled cture to dissolve the salt, and treatment with a slight excess of centrated hydrochloric acid precipitated 3-nitroanthranilic acid a bright yellow, crystalline powder (7·8 g.; 90%). The acid s obtained in fine, yellow needles, m. p. 208—209°, from hot er (Hübner, *loc. cit.*, gives m. p. 204°); in other respects the perties of the acid agree with those described by Hübner. duction of the acid with stannous chloride showed no indication he formation of a derivative of *m*-phenylenediamine, and hence absence of 6-nitroanthranilic acid.

-*Nitro*-2-*acetylaminobenzoic acid*, obtained by boiling the above el (2 g.) with acetic anhydride (4 c.c.) for 5 minutes, crystallised m hot water or acetic acid in bright yellow, silky needles, m. p. 8—181° (Found: N, 12·6. $C_9H_8O_5N_2$ requires N, 12·5%).

· *and* 5-*Nitrophthalamic Acids*.—A mixture of the ammonium

salts of these acids was obtained by dissolving 4-nitrophthal anhydride (60 g.) in warm aqueous ammonia (90 c.c.). The produ (50 g.), consisting of fine, white needles, melted at 190—192° wi decomposition, solidified, and remelted at 197—198°, having be converted into the imide (Bogert and Boroschek, *loc. cit.*, a Seidel and Bittner, *loc. cit.*, give m. p. of 4-nitrophthalimide 197° and 202°, respectively). The mixture of 4- and 5-nitr phthalamic acids was obtained in almost theoretical yield by ad tion of concentrated hydrochloric acid (40 c.c.) to the ammoniu salts (48 g.) in water (60 c.c.). Attempts to separate the acids we unsuccessful. The mixture melted at 150—155° with loss of wat resolidified and remelted at 198°, since both acids yield 4-nitr phthalimide.

4- *and* 5-*Nitroanthranilic Acids.*—A mixture of these acids w obtained by treating the above mixture of phthalamic acids (35 with standard hypochlorite solution (266 c.c.) as described in t previous case. Acidification of the resulting red solution gave mixture (22 g.; 73%) of yellow and orange particles, m. p. 250 260° (decomp.). A portion of the mixture (15 g.) was extract in a Soxhlet apparatus for 2 days with boiling xylene, which beca orange-red. The insoluble, pale yellow residue of 5-nitroanthrani acid, amounting to 60% of the original mixture, crystallised fr dilute alcohol in glistening, yellow needles, m. p. 280°, agreeing wi m. p. given by Seidel and Bittner (*loc. cit.*). The m. p. of 5-nitr anthranilic acid is also variously given as follows: 263° (Hübn *loc. cit.*); 270° (Rhalis, *Annalen*, 1879, **198**, 112); 261—263° (Kra *J. pr. Chem.*, 1896, **53**, 222); 263° (Rupe, *Ber.*, 1897, **30**, 109 269·5° (Ullmann and Uzbachian, *Ber.*, 1903, **36**, 1802). The a showed the characteristic reactions described in the literature 5-nitroanthranilic acid, and was converted into 5-nitro-2-acet aminobenzoic acid, melting at 216—217°, by boiling with ace anhydride. Seidel and Bittner (*loc. cit.*) and Ullmann and Uzbachi (*loc. cit.*) give, respectively, 214—215° and 221° as the melting po of the acetyl derivative.

The xylene solution obtained above left on evaporation a d orange, flaky mass (40% of the original mixture) of 4-nitroant anilic acid containing a little of its isomeride. Attempts to pur the acid by repeated crystallisation from alcohol as described Seidel and Bittner (*loc. cit.*) were unsuccessful, as the final prod melted indefinitely between 237—240°, and was evidently stil mixture. It was therefore converted into the acetyl derivative boiling with acetic anhydride for a few minutes. The crude prod melted at 190—195°, but after crystallising several times from dil alcohol, 4-nitro-2-acetylaminobenzoic acid was obtained in lo

lender needles, m. p. 217° (Seidel and Bittner, *loc. cit.*, give 188°; Wheeler and Barnes, *Amer. Chem. J.*, 1898, **20**, 229, give 215°). A solution of the acetyl compound in a small quantity of hot alcohol was boiled with a few c.c of concentrated hydrochloric acid; on cooling, pale yellow needles of the hydrochloride of 4-nitroanthranilic acid separated.

The hydrochloride was dissociated by water and the 4-nitroanthranilic acid produced crystallised from dilute alcohol in stout, deep orange prisms, m. p. 269° (Wheeler and Barnes, *loc. cit.*, Wheeler and Johns, *Amer. Chem. J.*, 1910, **44**, 443, and Seidel, *Ber.*, 1901, **4**, 4352, give the m.p. of 4-nitroanthranilic acid as 264°). 4-Nitroanthranilic acid was difficultly soluble in hot water, and on reduction with stannous chloride and hydrochloric acid gave an indication of the formation of a derivative of *m*-phenylenediamine.

It is desired to acknowledge a grant made to one of us (E. C.) by the Department of Scientific and Industrial Research, which enabled him to participate in this work.

THE UNIVERSITY, MANCHESTER. [*Received, May 19th*, 1925.]

CXXXVIII.—*Derivatives of δ-o-Aminobenzoylvaleric Acid.*

By MARGARET JOYCE PATERSON and SYDNEY GLENN PRESTON PLANT.

THE acid, m. p. 129°, obtained by Perkin and Plant (J., 1923, **123**, 778) and thought to be δ-*o*-aminobenzoylvaleric acid,

$$NH_2 \cdot C_6H_4 \cdot CO \cdot [CH_2]_4 \cdot CO_2H,$$

has been converted into δ-*o*-hydroxybenzoylvaleric acid, identical with the compound prepared by von Braun (*Ber.*, 1922, **55**, 3761) by the oxidation of hexahydrodiphenylene oxide, and its constitution thus proved.

δ-*o*-Aminobenzoylvaleric acid cannot be made to yield a phenylhydrazone, oxime, or semicarbazone under the usual conditions, but the corresponding derivatives of δ-*o*-hydroxybenzoylvaleric acid are readily obtained.

δ-*o*-Benzoylaminobenzoylvaleric acid is converted by alkalis into δ-*o*-aminobenzoylvaleric acid and a small quantity of γ-4-hydroxy-2-phenylquinoline-3-butyric acid (Perkin and Plant, *loc. cit.*). We now find that δ-o-*acetylaminobenzoylvaleric acid* gives better yields of the corresponding γ-4-*hydroxy*-2-*methylquinoline*-3-*butyric acid* as well as some δ-*o*-aminobenzoylvaleric acid. δ-o-*Formylaminobenzoylvaleric acid*, on hydrolysis under various

conditions, gave exclusively δ-*o*-aminobenzoylvaleric acid, no trace of a quinoline derivative being detected.

Experimental.

δ-o-*Hydroxybenzoylvaleric Acid.*—The diazo-solution prepared from δ-*o*-aminobenzoylvaleric acid (4 g.) in concentrated hydrochloric acid (20 c.c.) and water (40 c.c.) by means of sodium nitrite (1·3 g. in 15 c.c. of water) was heated on the steam-bath until nitrogen ceased to be evolved. The oil produced, which solidified on cooling, was boiled in dilute sodium hydroxide solution for 15 minutes with charcoal. δ-*o*-Hydroxybenzoylvaleric acid, obtained by acidifying the solution with hydrochloric acid, crystallised from petroleum in long, colourless needles, m. p. 94°; von Braun (*loc. cit.*) gives m. p. 94° (Found: C, 65·0; H, 6·3. Calc., C, 64·8; H, 6·3%).

The phenylhydrazone, prepared by warming the acid with an excess of phenylhydrazine for a few minutes and treating the mixture with dilute acetic acid, had, after recrystallisation from aqueous alcohol, the m. p. (173°) recorded by von Braun.

δ-o-*Acetylaminobenzoylvaleric Acid.*—A mixture of δ-*o*-aminobenzoylvaleric acid with twice its weight of acetic anhydride was heated on the steam-bath for an hour, the excess of acetic anhydride removed under reduced pressure, and the residue poured into water. The viscous product was boiled in alcohol with charcoal, and the δ-o-*acetylaminobenzoylvaleric acid* precipitated, after filtration, by the gradual addition of water was recrystallised from aqueous alcohol, separating in colourless plates, m. p. 153° (Found: C, 64·1; H, 6·7. $C_{14}H_{17}O_4N$ requires C, 63·9; H, 6·5%).

A solution of δ-*o*-acetylaminobenzoylvaleric acid (2 g.) and potassium hydroxide (5·5 g.) in water (35 c.c.) was heated for an hour on the steam-bath, cooled, acidified with hydrochloric acid and the small colourless precipitate removed. The filtrate yielded δ-*o*-aminobenzoylvaleric acid on successive treatment with potassium hydroxide and acetic acid. The small precipitate was recrystallised from alcohol, when γ-4-*hydroxy*-2-*methylquinoline*-3-*butyric acid* was obtained in colourless prisms, m. p. 241° (Found: N, 5·7. $C_{14}H_{15}O_3N$ requires N, 5·7%).

δ-o-*Formylaminobenzoylvaleric Acid.*—δ-*o*-Aminobenzoylvaleric acid (3 g.) was heated with formic acid (6 g.) on the steam-bath for 3 hours under reflux, the excess of formic acid was then allowed to escape, and the residue yielded a colourless solid on rubbing with alcohol. The product was recrystallised from alcohol and δ-*o*-*formylaminobenzoylvaleric acid* separated in colourless plates, m. p. 160° (Found: N, 5·5. $C_{13}H_{15}O_4N$ requires N, 5·6%).

One of us (S. G. P. P.) wishes gratefully to acknowledge the receipt f a grant from the Chemical Society Research Fund which has efrayed a part of the cost of this investigation.

The Dyson Perrins Laboratory,
Oxford. [*Received, June 13th*, 1925.]

CCXXXIX.—*Bismuth Dihydride.*

By Edward Joseph Weeks and John Gerald Frederick Druce.

Having prepared solid hydrides of arsenic (*Chem. News*, 1924, **129**, 1) and antimony (this vol., p. 1069), we turned our attention to he analogous solid bismuth dihydride. The method of preparation vas similar to one employed in the case of antimony dihydride. A olution of bismuth chloride in hydrochloric acid was added radually to a mixture of zinc (free from iron, carbon, and arsenic) nd fairly strong hydrochloric acid which was rapidly evolving ydrogen. At each addition of bismuth chloride the evolution of as slackened and could even be made to stop altogether until the ismuth chloride was converted into a flocculent, grey precipitate : $BiCl_3+8H=Bi_2H_2+6HCl$. When all the zinc (which was used in xcess) had dissolved, the liquid was rapidly filtered in an atmo- phere of hydrogen, and the precipitate washed many times, first with ot strong hydrochloric acid, then with hot dilute acid, and finally ith water until the wash water was neutral. The residue was rained and dried, first in hydrogen and finally in a vacuum esiccator over concentrated sulphuric acid.

On heating in a vacuum, bismuth dihydride gave off hydrogen nd left metallic bismuth—quite different from the amorphous ihydride. 0·9184 G. gave 44 c.c. H_2, measured at *N.T.P.*, and ·9144 g. Bi : H, 0·45; Bi, 99·57. 1·4606 G. lost 0·0088 g. H_2 : Bi, 99·39; H, 0·60. On combustion 0·4849 g. gave 0·0235 g. H_2O : I, 0·54 (Bi_2H_2 requires Bi, 99·52; H, 0·48%).

The volume of hydrogen produced was determined as follows : he apparatus, with a quicklime tower in series, was twice filled ith nitrogen (previously passed over red-hot copper) and exhausted s completely as possible. The pressure (p) was noted, and the ihydride heated until there was no further pressure change. The nal pressure (P) was noted, the apparatus re-exhausted until the ressure was p, and nitrogen, measured at atmospheric pressure, dded until the pressure P was restored.

Bismuth dihydride, heated in a tube in absence of air, gave a irror of bismuth just beyond the heated zone. It thus appeared hat the dihydride might decompose into bismuth and bismuthine :

$3Bi_2H_2=2BiH_3+4Bi$. (On heating, cuprous hydride decomposes into copper and cupric hydride [Barlett and Merrill, *Amer. Chem. J.*, 1896, **17**, 185], and arsenic dihydride into arsenic and arsine [Moser and Brukl, *Monatsh.*, 1924, **45**, 25]). To test this supposition, bismuth dihydride was heated in a stream of purified hydrogen. The issuing gas produced in silver nitrate solution a grey precipitate soluble in nitric acid. This was presumably silver bismuthide, as its nitric acid solution, after removal of silver as chloride, gave with hydrogen sulphide a dark brown precipitate, the solution of which in warm dilute nitric acid deposited bismuth hydroxide on addition of ammonia.

Bismuth dihydride prepared as described above was free from zinc, carbon, and iron, but contained a trace of chlorine (less than 0·02%, estimated by Volhard's method).

Fused potassium nitrate reacted very vigorously with the dihydride (as with antimony dihydride), but only slowly oxidised finely divided bismuth.

BATTERSEA GRAMMAR SCHOOL,
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CCXL.—*The Nature of the Alternating Effect in Carbon Chains. Part III. A Comparative Study of the Directive Efficiencies of Oxygen and Nitrogen Atoms in Aromatic Substitution.*

By ERIC LEIGHTON HOLMES and CHRISTOPHER KELK INGOLD.

THAT directive action in aromatic substitution is the result of an alternating effect transmitted throughout the ring from a key-atom is generally agreed, and a convincing confirmation has recently been given by Pyman and Stanley (J., 1924, **125**, 2484; compare *Ann. Report*, 1924, pp. 110—111). It is the authors' hope to elucidate more precisely the nature of the alternation, and to discover, by the close study of different key-atoms, what property of them it is that is so effectively propagated.

In Part I (this vol., p. 513) it was stated (and this is the starting point of the present investigation) that whilst Kermack and Robinson's hypothesis of an induced electropolar effect requires that oxygen, owing to the greater pre-formation of its octet, should predominate over nitrogen as a negative key-atom,* the theory of alternating free and bound affinity demands that the more unsaturated element, tervalent nitrogen, should have greater influence.

* For references see Part I.

From this theoretical distinction there followed a difference in the predicted orienting effect of the nitroso-group, which was determined, and found to be in agreement with the affinity theory. It was then suggested, however (compare Part II, this vol., p. 870),

(1) that a group with two competing negative atoms constituted a case too complicated for prediction by the polarity principle * (Lapworth),

(2) that the observed facts could be accommodated by means of a different point of view when the atom united to the ring contained a " lone pair " of electrons (Robinson).

A group was therefore examined which (*a*) contained only one negative atom, oxygen, (*b*) was joined to the benzene ring through carbon; and again results were obtained indicating that directive action depends on the unsaturation rather than the polar character of the atom producing it. Since these results were communicated, however, a further suggestion has been made (Robinson, *Chem. and Ind.*, 1925, **44**, 260) which fundamentally affects much of the work in progress. It is

(3) that atoms, previously regarded as negative, such as the oxygen atoms of ethers, may, upon occasion, act as *positive* key-atoms by functioning as " onium " elements.†

Such an occurrence would obviously reverse all the effects to be expected on the basis of the polarity theory, which could thus, in a given case, be reconciled with results otherwise opposed to it.

A series of experiments has therefore been instituted which, while still adhering to conditions (*a*) and (*b*) imposed by the earlier arguments of Lapworth and Robinson (1) and (2), in addition exercises a definite control over the suggestion that " onium " action may account for the exceptions to the polar hypothesis.‡

In order to understand the method employed it is necessary to consider the position of toluene and its monosubstituted products with regard to the principles both of alternating affinity and of alternate polarities.

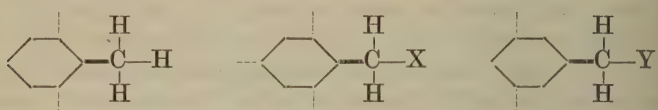
It is fundamental to the affinity theory (compare Flürscheim, *Z. pr. Chem.*, 1907, **76**, 197; *Chem. and Ind.*, 1925, **44**, 249) that carbon exerts valencies of more, or less, than the normal affinity content only when compelled to do so by the varying requirements of an unsaturated, or over-saturated, attached atom or group

* That of 1920 was referred to.

† For example, by forming salts with the reagent employed.

‡ Yet another argument (4), recently advanced by Lapworth, is alluded to below (p. 1808).

(mechanism of propagation). In toluene, the phenyl group is unsaturated (possesses residual affinity), and hence the methyl carbon atom is strongly bound, a condition leading to *op*-substitution (I). If, now, one of the methyl hydrogen atoms is replaced by a feebly unsaturated atom (X), the demand made by this atom on the affinity of the carbon atom may be insufficient to counterbalance the unsaturation of the phenyl group, and again *op*-substitution will be the rule (II). On the other hand, if, in place of X, a strongly unsaturated atom (Y) be introduced, then the unsaturation of the phenyl group may be overcome, when a condition will arise leading to *m*-substitution (III):



(I.) (II.) (III.)

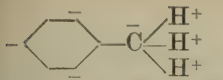
Now bivalent oxygen is a feebly unsaturated atom, whilst tervalent nitrogen is strongly unsaturated. Hence, if we consider comparatively benzyl alcohols (IV) and benzylamines (V) (using these terms in a general sense to include alkyl and acyl derivatives, etc.), the former should be more closely represented by condition (II), and the latter by condition (III):

(IV.) C_6H_5—CH_2—OA $\qquad$ C_6H_5—CH_2—NAA′ (V.)

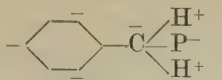
That is to say, the benzylamines should show a greater tendency than the benzyl alcohols towards *m*-direction, as against *op*-direction. Of course, if oxonium or ammonium salt-formation were to take place *op*-direction might result, but, whilst benzyl alcohols should exhibit *op*-direction *in any event*, benzylamines should show *m*-direction if and when salt formation does not occur. *It is still true, therefore, that according to the affinity theory derivatives of benzylamine should show a greater tendency towards* m-*substitution, and a smaller tendency towards* op-*substitution, than the benzyl alcohols, and that* m-*directive action should never prevail amongst the latter.*

On the other hand, according to polarity principles, hydrogen is feebly key-positive (Lapworth, *Mem. Manchester Phil. Soc.*, 1920, **64**, No. 3, p. 5); thus, the *op*-substitution of toluene may be explained (VI). If, now, in place of one of the methyl hydrogen atoms a weakly negative atom (P) be introduced, this may conceivably be insufficient to counterbalance the effect of the two remaining hydrogen atoms, and, in this case, *op*-substitution will still prevail (VII). If, however, a strongly negative atom (Q) is

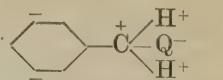
ntroduced, the influence of the hydrogen atoms should be over-come and *m*-direction should ensue (VIII).



(VI.)



(VII.)



(VIII.)

Now, if the oxygen atom in benzyl alcohols acts as a negative key-atom, it must be assumed to be like " P " rather than like " Q," for benzyl alcohol derivatives display *op*-substitution (see below). It follows, however, from the electronic principles alluded to at the commencement that if *oxygen* is not negative enough effectively to control substitution from the position it occupies in the benzyl alcohols, then, *a fortiori*, more feebly negative *nitrogen* in the same position will be unable to do so. Assuming, then, that we have to do with *negative* key-atoms in both cases, there should be a greater tendency to *op*-substitution, and a smaller tendency to *m*-substitution, amongst benzylamines than amongst benzyl alcohols.

Let it now be supposed that these elements act in their " onium " forms, that is, as *positive* key-atoms. This would supply a convenient explanation of *op*-substitution in benzyl alcohols, since the methyl carbon atom would now be attached to three positive atoms as in toluene. But the same principles which require that oxygen shall be more effective than nitrogen as a negative key-atom also demand that nitrogen shall be more powerful when both are positive (Robinson, *loc. cit.*). Hence, in this case also, benzylamines should show the greater tendency to *op*-substitution.

The only remaining case is that which would arise if, under the condition of substitution, oxonium salts could not be formed, whilst the more stable, analogous, ammonium salts could; oxygen would then be a negative key-atom, but nitrogen might be a positive one. Obviously, however, the expected differences would, in this case, *still* be in the sense previously stated, only greater. *Thus, in all three cases, polarity principles require that benzylamines shall show a greater tendency to* op-*substitution, and a smaller tendency to* m-*substitution, than benzyl alcohols.*

It follows, then, that in the comparison of benzyl alcohols with benzylamines we have a clear issue, from which the theory of " onium-action " provides no exit.

Before the commencement of this investigation several observations had already been made indicating the prevalence of *op*-substitution in benzyl alcohol derivatives of the type $C_6H_5 \cdot CH_2 \cdot O \cdot A$. Thus Beilstein and Kühlberg (*Annalen*, 1868, **147**, 341) obtained

p-nitrobenzyl acetate by direct nitration of benzyl acetate (A = ·CO·CH_3), whilst Staedel (*Annalen*, 1883, **217**, 177) prepared several *p*-nitrobenzyl derivatives by the nitration of benzyl phenyl ethers and benzyl tolyl ethers (A = Aryl).

These results have now been generalised by the study of a number of new cases, chosen in such a way as to give oxonium salt formation, if it occurs, the greatest possible opportunity to manifest its effects.

As is well known, the stability of ammonium salts (and, it may be assumed, of "onium" salts in general) is diminished by the introduction of an acyl group in the place of an alkyl group (compare the basicity of acetanilide with that of methylaniline); and the greater the strength of the acid from which the acyl group is derived, the more completely is the salt formation suppressed. It might therefore be supposed that even if oxonium salt formation, resulting in "positive" oxygen, is the cause of the *op*-substitution of benzyl ethers (A = Alkyl), the tendency to this type of substitution would become less marked in benzyl esters of weak acids (*e.g.*, benzyl acetate; A = ·CO·CH_3), and non-existent in benzyl esters of strong mineral acids (*e.g.*, benzyl nitrate; A = ·NO_2), since an anhydro-union with strong mineral acids, like nitric acid and sulphuric acid, is known to suppress the ammonium salt formation of even comparatively strong nitrogen bases.

Cases have therefore been selected in such a way as to furnish examples of all these three classes; and in every case it has been found that substitution occurs mainly or exclusively in the para-position; *m*-substitution has in no instance been observed, despite the variation in the character of "A."

The examples on which the above general statement is based are collected together in the following table. They afford, it is believed, strong grounds for the conclusions (a) *that* op-*substitution prevails amongst benzyl alcohol derivatives of the type* C_6H_5–CH_2–OA, *whether A = alkyl or acyl;* (b) *that oxonium salt formation with the reagent employed is not the cause of this phenomenon.*

TABLE I.

C_6H_5–CH_2–OA (class).	A·OH.	Result.	Reference.
A = alkyl	*s*-Tribromophenol	*p*	This paper.
	mm-Dinitro-*p*-cresol	*p*	Staedel (*loc. cit.*).*
A = acyl (A·OH = weak acid)	Acetic acid	*p*	Beilstein and Kühlberg (*loc. cit.*).
A = acyl (A·OH = strong acid)	Picric acid	*p*	This paper.
	Nitric acid	*p*	,, ,,

* Staedel also nitrated the ethers in which A = phenyl, *o*-tolyl, and *p*-tolyl. In each of these cases nitro-groups entered both rings, but that which entered the benzyl group did so in the *p*-position.

In the case of the benzylamines the only compounds of the type $C_6H_5 \cdot CH_2 \cdot NAA'$ which have been examined (so far as we have ascertained) in regard to ring substitution prior to this investigation are (i) acetobenzylamide (A = H; A′ = $\cdot CO \cdot CH_3$) and (2) phenylethylbenzylamine (A = Et; A′ = Ph). Acetobenzylamide was found by Amsel and Hofmann to nitrate in the *p*-position (*Ber.*, 1886, **19**, 1286), a result which we have confirmed. Phenylethylbenzylamine was stated by Schultz and Bosch (*Ber.*, 1902, **35**, 1292) to nitrate in the *m*-position in the benzyl group; but doubt has been cast on this result (Flürscheim, *Chem. and Ind.*, 1925, **44**, 285), a doubt which is increased by the investigation recorded in this paper of the closely analogous case of methyldibenzylamine (A = Me; A′ = CH_2Ph).* It was apparent at the outset, therefore, that no general conclusion with regard to the substitution of benzylamine could be reached on the basis of previously recorded observations, and that before the comparison with benzyl alcohols could be made a series of experiments on representative benzylamines was necessary.

Such a series has now been carried out, and, in contrast to the results obtained with the benzyl alcohols $C_6H_5 \cdot CH_2 \cdot OA$, it has been found that predominant *m*-substitution is of common occurrence amongst derivatives of benzylamine, $C_6H_5 \cdot CH_2 \cdot NAA'$.

As in the previously described experiments, examples were selected in such a way as to obtain a maximum of control over effects due to ammonium salt formation.

The effects to be expected from this cause may be inferred from the case of aniline. As Bamberger has shown (*Ber.*, 1895, **28**, 399), aniline nitrate, $C_6H_5 \cdot NH_3 \cdot O \cdot NO_2$, which is *m*-orienting, readily loses water under ordinary nitration conditions, giving the nitroamine $C_6H_5 \cdot NH \cdot NO_2$, which, being insufficiently basic to form a stable salt, substitutes in the *op*-positions; hence arise the different results obtained with different concentrations of nitric acid. Now according to the theory of alternating free and bound affinity the nitrogen atom in benzylamine should direct oppositely to that in aniline when both are in analogous states of combination. Hence it might be expected that under ordinary conditions (concentrated nitric acid in the cold) the conversion of the nitrate $C_7H_7 \cdot NH_3 \cdot O \cdot NO_2$ into a non-basic nitroamine, $C_7H_7 \cdot NH \cdot NO_2$, would determine predominant substitution in the *m*-position. Actually this is what occurs, and, apart from analogy with aniline, there are four inde-

* We have not, however, repeated the experiments of Schultz and Bosch, since Prof. Robinson has recently announced his intention of doing so (*Chem. and Ind.*, 1925, **44**, 227).

pendent experimental reasons for concluding that it takes place in the manner suggested.

First, under the conditions stated, the *m*-nitro-derivative, although the main product (about 80%), is not the only one; a certain quantity of *p*-isomeride is also formed, and (possibly) a trace of ortho. If the explanation given is correct, this must mean that, at the temperature employed (0° to 20°), only a part of the benzylamine nitrate is dehydrated to benzylnitroamine. But an increase of temperature would easily complete this reaction and should thus suppress the by-products of the nitration. This was found to be the case: on nitration at temperatures approaching 100° the *m*-nitro-compound was obtained as sole product and in practically quantitative yield.*

Secondly, it follows from the explanation given that the phenomena observed with benzylamine should be reproduced in secondary benzylamines, $C_7H_7{\cdot}NHAlk$, but should disappear in tertiary derivatives, $C_7H_7{\cdot}N(Alk)_2$, since these lack the amino-hydrogen atom necessary for dehydration of the salt to the nitroamine. This was also observed, exactly as predicted: methylbenzylamine, $C_7H_7{\cdot}NH{\cdot}CH_3$, and dibenzylamine, $C_7H_7{\cdot}NH{\cdot}C_7H_7$, behave like benzylamine, directing mainly or exclusively towards the *m*-position, according to temperature; methyldibenzylamine, however, $(C_7H_7)_2NMe$, showed no tendency towards *m*-direction, but, on the contrary, gave *op*-products.

Thirdly, since the introduction of one acyl group into a primary amine greatly increases the difficulty of replacing the second amino-hydrogen atom by another acyl group, the prior mono-acylation of a benzylamine should prevent the formation under nitration conditions of a nitroamine, excepting, perhaps, at high temperatures. Now benzylamines are strong bases, and hence, if the acyl group introduced is derived from a weak acid, the substituted amide should be definitely basic, and it is true that acetobenzylamide, acetodibenzylamide, and acetomethylbenzylamide form moderately stable salts with mineral acids. Substitution in these compounds should therefore take place mainly, if not exclusively, through their salts, that is, in the *op*-positions. Further, since acetodibenzyl-

* This temperature effect may be contrasted with that observed in the sulphonation of aniline, which gives *m*-sulphanilic acid in the cold (substitution of sulphate) but *p*-sulphanilic acid at higher temperatures (the sulphate passing into the sulphamic acid under these conditions). Thus an increase of temperature causes a *p*-product to appear in the place of *m*-, in the case of aniline, but a *m*-product in the place of *p*-, when the directing nitrogen atom is one place further from the nucleus, as in benzylamine—a clear illustration, similar in some respects to that given by Pyman and Stanley (*loc. cit.*), of the essentially *alternating* character of the effect transmitted.

mide, $(C_7H_7)_2NAc$, is a definitely weaker base than methyldi-enzylamine, $(C_7H_7)_2NMe$, larger quantities of *m*-by-products ould be produced in the former case than in the latter. Again, nce acetobenzylamide and acetomethylbenzylamide are stronger ases than acetodibenzylamide, the last should yield the largest uantity of *m*-compound. Again, in the case of the very feebly asic acetodibenzylamide, the addition of different quantities of ater to the nitric acid used in the nitration should, by altering ie degree of hydrolysis of the salt, change the proportion of by-roducts: the more dilute the acid, the greater should be the roportion of *m*-product obtained. All these predictions have een verified in every detail.

Fourthly, diacetylbenzylamine, $C_7H_7{\cdot}N(CO{\cdot}CH_3)_2$, is non-basic, nd it obviously cannot form a nitroamine; it must therefore itrate as such. It follows that if *m*-substitution in benzylamine erivatives depends essentially on tervalent nitrogen, then this iacetyl compound, unlike the monoacetyl derivatives previously ientioned, should undergo substitution wholly or mainly in the -position. This was found to be the case.

These results, which are summarised in the following table, ive strong grounds * for the conclusion that *not only is* m-*substi-ution a frequent experience with benzylamine derivatives,*

$$C_6H_5{\cdot}CH_2{\cdot}NAA',$$

ut that it prevails in every case in which substitution through a salt precluded.

TABLE II.

Substance.	Main product.	By-product.	Reference.
enzylamine	*m*	*p*†	This paper.
ethylbenzylamine	*m*	*p*†	,, ,,
ibenzylamine	*m*	*p*†	,, ,,
ethyldibenzylamine	*p* (*o*)	—	,, ,,
cetobenzylamide	*p*	*m*?	Amsel and Hofmann (*loc. cit.*).
cetomethylbenzylamide...	*p*	*m*?	This paper.
cetodibenzylamide	*p* (*o*)	*m*	,, ,,
iacetylbenzylamine	*m*	—	,, ,,

† Only perceptible at low temperatures.

Comparing now the benzyl alcohols and benzylamines, we see iat, as the affinity theory demands, compounds of the former ass belong exclusively to the *op*-directing series, whilst those of ie latter display a strong tendency to *m*-substitution. Polarity

* For the sake of maintaining the strict comparison with benzyl alcohol erivatives, no use is here made of the few known instances of ring-sub-itution in benzylamines already substituted in the benzyl group, although ie data are consistent with the results now described.

principles, as shown above, require a difference of precisely th opposite kind.

In Part II * (*loc. cit.*) a peculiarly substituted benzyl ether wa examined in which the two side-chain hydrogen atoms of th ordinary benzyl group were removed from possible competitio with the oxygen atom by replacing them by a doubly-bound methyl ene group, $:CH_2$. The compound was α-methoxystyrene,

$$C_6H_5\cdot C(OMe):CH_2,$$

and some importance was attached to the case because it indicate in a particularly clear manner that *unsaturation*, rather tha negative character, is the cause of directive action. Recently however, a new suggestion, additional to those mentioned abov (1, 2, and 3, p. 1801), has been advanced. It is

> (4) that the unsaturated group, C:C, *itself* might behave a a " negative " key-group in the sense of the polarity rule, an hence in methoxystyrene act as would an oxygen atom directl attached to the benzene nucleus (Lapworth, *Chem. and Ind.* 1925, **44**, 228, 398).

We express no opinion as to the *a priori* probability of thi suggestion, but wish to point out that it (like every argument which has been advanced in defence of the polarity theory sinc these investigations were commenced) has been taken into seriou account in devising the experiments now described. It is com pletely answered. For if the *op*-direction of methoxystyrene is du to the " negative " double bond, why does it persist, against th polar principles cited above, when that double bond is absent, as i the benzyl ethers, $C_6H_5\cdot CH_2\cdot OA$? The cause lies not in the tw hydrogen atoms (pp. 1802—1803, 1807, 1808), nor in a " positive " oxygen atom (pp. 1804—1805, 1807), nor in the group A (pp. 1804— 1805, 1805—1807); for if it did, the *m*-direction of analogou benzylamines could not be explained. The same difficulty confront any attempt to base an explanation, or argument,‡ on the " dampin

* On p. 871, lines 11–12, " two intrinsically negative atoms in competitio for the function of key-atom " should be read in place of " two competin negative key-atoms," since the ellipsis used has caused misunderstanding.

† General arguments, such as the imputation of " insisting that any aton you like to choose must be a key-atom " (Robinson, *Chem. and Ind.*, 1925 **44**, 227), we regard as not justified in view of the full reasons that hav invariably been given for each assumption made. Arguments of this kin are excepted from the statement to which this footnote refers.

‡ The relevance to the polarity theory of the cases under discussion wa admitted by Robinson when predicting, on the basis of his theory, th position of substitution of the benzylamine examined by Schultz and Bosc (p. 1805); which should obviously yield *op*-substitution derivatives accordin to *any* of the theories discussed in this paper.

tion " of the saturated carbon atom (Robinson, *Chem. and Ind.*, 25, **44**, 148; Lapworth, *ibid.*, p. 398), or on lack of " conjugation " the key-atom with the nucleus.

It seems to us that there is only one *consistent* explanation of ese facts, namely, that which has uniformly and correctly fore- ld events throughout this series of investigations. Proof has en given that the efficiencies of " negative " key-atoms stand, not the order of their electron affinities, but in the order of their saturation; and it seems fair, therefore, to conclude that un- turation is the property transmitted. This is the essence of ürscheim's form of the alternating theory. We are aware that identifying unsaturation with potentially mobile electrons, and alternating distribution with a similarly propagated electronic splacement, a nearly equivalent theory may be formulated * ompare Robinson, *Chem. and Ind.*, 1924, **43**, 1297; 1925, **44**, 8; this vol., p. 370). But this cannot add validity to the ndamental idea, nor can it inspire enhanced confidence whilst e interpretation of the chemical terms remains speculative. We ggest, therefore, without denying the possibility of polar altern- ion, that the facts thus far adduced constitute grounds for the nclusion that the propagation of alternating unsaturation is the ime directive process in ordinary aromatic substitution.

Experimental.

(*A*) *Nitration of Benzyl Ethers and Esters.*

(i) s-*Tribromophenyl Benzyl Ether*, $C_6H_2Br_3{\cdot}O{\cdot}CH_2Ph$.—Equi- olecular quantities of benzyl chloride and *s*-tribromophenol were ded to a suspension of sodium ethoxide in boiling toluene, the tered solution was evaporated, and the residue recrystallised om alcohol. The product, m. p. 86—87°, had the properties scribed by Auwers (*Annalen*, 1907, **357**, 92).

For the nitration, the ether was added in small quantities to ncentrated nitric acid at about — 5°, the solution kept for 1 hour, ured on to ice, and the solid obtained, after draining from a nall quantity of adhering oil, crystallised from alcohol, when it parated in small prisms, m. p. 145° (Found : N, 3·1. $C_{13}H_8O_3NBr_3$ quires N, 3·0%). An impure by-product was obtained of higher trogen content.

s-*Tribromophenyl* p-*nitrobenzyl ether*, $C_6H_2Br_3{\cdot}O{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$, th which the above substance was identified, was prepared for mparison by the interaction of *p*-nitrobenzyl chloride and sodium ribromophenoxide in benzene solution. It separated in a moder-

* It involves, however, a reversal of postulated key-atom efficiencies.

ately pure form when ligroin was added to the filtered and evaporate liquid.

(ii) op-*Dinitrophenyl Benzyl Ether*, $C_6H_3(NO_2)_2 \cdot O \cdot CH_2Ph$.—Thi compound, which was prepared by Kumpf's method (*Annalen* 1884, **224**, 131), was nitrated under the conditions used in th previous experiment; on addition of ice a precipitate was obtaine which, twice crystallised from benzene, gave well-defined, orange yellow needles, m. p. 198°, of *op*-dinitrophenyl *p*-nitrobenzyl ethe (Staedel, *loc. cit.*; Kumpf, *loc. cit.*). The latter method, using however, *p*-nitrobenzyl chloride in place of the iodide, and heatin in the absence of a solvent at 150°, was employed in order to obtai a specimen for comparison.

(iii) *Benzyl Nitrate*, $C_6H_5 \cdot CH_2 \cdot O \cdot NO_2$.—Prepared from benzy chloride and silver nitrate by Nef's method (*Annalen*, 1889, **309** 171), and isolated and purified by distillation in a vacuum, thi substance, which, after twice distilling, had b. p. 101—105°, wa analytically pure, and free from halogen, was run during abou 4 hours through a fine capillary tube into seven times its weigh of 95% nitric acid at about −10°, and the solution immediatel poured on to ice. The oil thus precipitated slowly solidified, an the solid, which was drained on porous porcelain and crystallise from warm aqueous alcohol, was identified as *p*-nitrobenzyl nitrat by its m. p. (71°) and by direct comparison with a specimen prepare by Nef's method from *p*-nitrobenzyl chloride and silver nitrate. O oxidation with 3% alkaline permanganate solution (equiv. to rathe more than 2O) at about 100°, *p*-nitrobenzoic acid was obtained.

A considerable amount of oxidation took place during attempt to nitrate benzyl ethyl ether, and even more in the case of benzy alcohol. The attempts were therefore abandoned.

(B) *Nitration of Primary, Secondary, and Tertiary Benzylamines and of certain Mono- and Di-acetyl Derivatives.*

(iv) *Benzylamine*.—This was prepared from potassium phthal imide and benzyl chloride by Gabriel's method (*Ber.*, 1887, 20 2227), but the tedious process of hydrolysing the phthalobenzyl imide with hydrochloric acid in sealed tubes was replaced by th following two-stage method, which is conveniently carried ou with larger quantities of material. The phthalobenzylimide i boiled for ½ hour with half its weight of potassium hydroxide ir 10% aqueous solution. The *phthalobenzylamic acid*,

$$CH_2Ph \cdot NH \cdot CO \cdot C_6H_4 \cdot CO_2H,$$

produced on acidification crystallises from alcohol in slender needles m. p. 155° (Found: C, 70·0; H, 5·1. $C_{15}H_{13}O_3N$ requires C, 70·3 N, 5·1%).

The crude amic acid was boiled for 18 hours with 20% hydrochloric acid (3 parts), the phthalic acid removed from the cooled solution, and the filtrate evaporated to dryness. The benzylamine isolated from the residue of hydrochloride by means of ether and sodium hydroxide was purified by distillation.

Another method, also a convenient one for the preparation of large quantities, consists in warming in chloroform solution a mixture of equal weights of hexamethylenetetramine and benzyl chloride, and hydrolysing the product with a mixture of concentrated hydrochloric acid and 95% alcohol (1 : 3 by volume).

Nitration of Benzylamine at Different Temperatures.—The general results of the experiments on the nitration of benzylamine at temperatures ranging from $-10°$ to 105° have already been described. The experiments were all carried out, so far as possible, under comparable conditions as to strength and amount of nitric acid. Details of two illustrative cases are given below.

(*a*) Benzylamine (2 g.) was run through a capillary tube during 3 hours into 10 c.c. of 95% nitric acid cooled to $-10°$. After remaining for 1 hour at this temperature, the product was mixed with ice. The crystals (1·4 g.) which separated during the next few hours consisted of almost pure *m*-nitrobenzylamine nitrate, m. p. 210° (the correct m. p. being 214°; see below). The filtrate was made alkaline with sodium hydroxide and extracted with ether, the extract shaken with a small excess of 2*N*-nitric acid, and the aqueous solution of nitrates evaporated. From the mixture thus obtained a further quantity of *m*-nitrobenzylamine nitrate was readily isolated by fractional crystallisation. The *p*-isomeride, which was also present, could not be fully purified, however, and the more soluble nitrates were therefore converted into the free bases, and these were acetylated with acetic anhydride in the usual manner. Crystallisation from water readily gave the pure acetyl derivative of *p*-nitrobenzylamine. The presence of an *ortho*-compound in the ultimate residues of this and similar experiments was suspected, but could not be definitely established owing to the smallness of the quantity.

(*b*) Benzylamine was added quickly to nitric acid at 100° and the product worked up in the manner just described. The yield of *m*-nitrobenzylamine nitrate was practically quantitative; no trace of the *p*- or *o*-compound could be detected.

o-, *m*-, and *p*-Nitrobenzylamines, which have not been previously described, were prepared by methods which determined their constitution.

o-*Nitrobenzylamine.*—A mixture of *o*-nitrobenzyl chloride (5 g.)

with 10% alcoholic ammonia (50 c.c.) was shaken for 2 hours and kept until the deposition of solid matter ceased (1—2 weeks). The solution was filtered and evaporated, and the residue, which was partly solid and partly liquid, lixiviated with water, in which the solid portion dissolved. On evaporation of this aqueous solution to dryness a well-crystallised hydrochloride was obtained, from which o-*nitrobenzylamine*, a colourous oil, was extracted with ether after the addition of sodium hydroxide. The base could not be induced to crystallise and was therefore characterised by means of its salts and acetyl derivative.

The *hydrochloride* separated from water in colourless needles, m. p. 248° (Found: Cl, 18·6. $C_7H_9O_2N_2Cl$ requires Cl, 18·8%), and the *nitrate* from the same solvent in small, white prisms, m. p. 173—174° (decomp.).

m-*Nitrobenzylamine*.—This was prepared from *m*-nitrobenzyl chloride by the same method and was obtained as a colourless oil which refused to crystallise.

The *hydrochloride* crystallised from water in large, colourless leaflets, m. p. 250°; and the *nitrate* in colourless, flattened needles, m. p. 214° (decomp.) (Found: C, 39·1; H, 4·2. $C_7H_9O_5N_3$ requires C, 39·1; H, 4·3%).

p-*Nitrobenzylamine*.—This was prepared in a like manner from *p*-nitrobenzyl chloride, but could not be induced to solidify. It was identified by means of its known acetyl derivative, a specimen of this being prepared for comparison by the method of Amsel and Hofmann (*loc. cit.*). The free base was further characterised by its *hydrochloride*, which separated from ethyl alcohol in colourless, flattened needles, m. p. 224° (Found: Cl, 18·9. $C_7H_9O_2N_2Cl$ requires Cl, 18·8%); and its *nitrate* crystallised from water in yellow plates, m. p. 180—181°.

(v) *Methylbenzylamine*, $C_6H_5{\cdot}CH_2{\cdot}NHMe$.—The preparation of this substance in quantity by methods given in the literature presented initial difficulties, but two satisfactory methods were ultimately obtained, one a modification of Hinsberg's process, and the other depending on the regulated interaction of benzyl chloride with methylamine.

(*a*) p-*Toluenesulphonbenzylamide*, $CH_3{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}CH_2Ph$.—Benzylamine (20 g.) was dissolved in dry pyridine and 40 g. of *p*-toluenesulphonyl chloride were added cautiously and with shaking. The mixture, which became hot and of a deep red colour, was kept for 1 hour and then poured into water. The oily precipitate, which solidified on rubbing, was crystallised from alcohol, when long, stout, colourless prisms, m. p. 114°, were obtained (Found: N, 5·2. $C_{14}H_{15}O_2NS$ requires N, 5·37%).

p-Toluenesulphonbenzylmethylamide, $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NMe \cdot CH_2Ph$.—The above amide (40 g.), methyl iodide (80 g.), alcohol (20 c.c.), and aqueous sodium hydroxide were shaken together for about an hour, the sodium hydroxide being kept in sufficient excess to render the mixture strongly alkaline throughout the period. The mixture was heated on the steam-bath for 15 minutes and poured into water, and the oily precipitate, which solidified, was crystallised from alcohol, from which the pure benzylmethylamide separated in colourless plates, m. p. 95° (Found : N, 5·4. $C_{15}H_{17}O_2NS$ requires N, 5·1%).

Some difficulty was experienced in hydrolysing this substance, the convenient general process of warming with a mixture of acetic and sulphuric acids failing owing to the instability of the product under the conditions. Hydrolysis was, however, effected by heating the amide for 7 hours at 165—170° with 1·5 times its weight of concentrated hydrochloric acid. (Below 155°, the hydrolysis is extremely slow, whilst above 175° an extensive separation of carbon takes place.) The base was extracted with ether from the cooled, basified solution, and separated from neutral impurities by re-extraction with aqueous hydrochloric acid. It was finally recovered from the crystallised hydrochloride by extraction with ether in the presence of alkali, and purified by distillation.

(*b*) A mixture of benzyl chloride (20 g.), alcohol (200 c.c. of 95%), and aqueous methylamine (70 c.c. of 33% solution) was heated in a well-stoppered flask at 60° for an hour and allowed to cool. The alcohol was removed by distillation, the residue made alkaline and extracted with ether, and the extract dried with potassium carbonate and evaporated. The residue thus obtained, on distillation, yielded a large fraction, b. p. 180—200°, which on redistillation boiled almost completely at 184—186°, consisting of pure methylbenzylamine. The fraction boiling above 200° was heated with an excess of acetic anhydride for a few minutes, and then with water. The solution, after being made alkaline, was extracted with ether, and the extract washed with very dilute hydrochloric acid and then evaporated. The residue, on boiling for 12 hours with 20% hydrochloric acid, yielded a further quantity of methylbenzylamine hydrochloride, which was decomposed to give the free base.

The base prepared by any of these methods had b. p. 184—186°, and was characterised by means of its *hydrochloride*, which separated from ethyl alcohol in rosettes of needles, m. p. 195° (Found : Cl, 22·4. $C_8H_{12}NCl$ requires Cl, 22·5%).

Nitration of Methylbenzylamine at Different Temperatures.—Nitration at low temperature was conducted much as described for

the case of benzylamine, but no precipitation was obtained on the addition of ice. The product was therefore made strongly alkaline and extracted with ether, and the combined ethereal extracts were shaken several times with dilute hydrochloric acid. On evaporation of the acid solution crystals were not obtained until the whole of the solvent had been removed, when a solid remained which was recrystallised from ethyl alcohol. In this way a small quantity of a moderately soluble salt was easily separated from the large amount of a very soluble salt which accompanied it. The somewhat sparingly soluble salt, after twice crystallising, separated in colourless, flattened needles, m. p. 226°, which did not depress the m. p. of an authentic specimen (see below) of methyl-*p*-nitrobenzylamine hydrochloride. The readily soluble salt separated sometimes as laminæ and sometimes in rosettes of needles. After thrice crystallising, it melted at 181° and was identified as methyl-*m*-nitrobenzylamine hydrochloride by comparison and by the m. p. of a mixture with a genuine specimen (below). The yields of *p*- and *m*-isomerides were usually about 10% and 80% respectively, about 10% of the material being either lost during manipulation or not separated. Careful search was made for the *o*-compound, but this could not be isolated, and all the impure residues had their m. p.'s depressed by admixture with a specimen of pure methyl-*o*-nitrobenzylamine hydrochloride. When the nitration was conducted at temperatures approaching 100°, no *p*-isomeride was formed, the product consisting wholly of the *m*-nitro-compound.

Methyl-o-*nitrobenzylamine*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NHMe$.—After a mixture of *o*-nitrobenzyl chloride (5 g.), 95% ethyl alcohol (30 c.c.) and 33% aqueous methylamine (30 c.c.) had been kept for a week the solution was filtered and evaporated and the semi-solid residue mixed with dilute hydrochloric acid and evaporated to dryness. The oily base liberated from this hydrochloride refused to crystallise and was therefore identified through its hydrochloride, which when crystallised from water, formed small, pale yellow prisms having the m. p. (175°) and properties recorded by Gabriel and Jansen (*Ber.*, 1891, **24**, 3090).

Methyl-m-*nitrobenzylamine* was prepared from *m*-nitrobenzyl chloride and methylamine as described above, and as it was an oil which would not solidify, was characterised by means of its salts.

The *hydrochloride* separated from alcohol in small, colourless flattened needles, m. p. 182° (Found: Cl, 17·5. $C_8H_{11}O_2N_2Cl$ requires Cl, 17·4%), and the *nitrate* from dilute nitric acid in long flattened needles, m. p. 150°.

Methyl-p-*nitrobenzylamine* was also obtained as an oil and char

terised by its *hydrochloride*, flattened needles, m. p. 226° (Found : 17·5. $C_8H_{11}O_2N_2Cl$ requires Cl, 17·4%).

(vi) *Dibenzylamine*, $(C_6H_5{\cdot}CH_2)_2NH$: *Nitration at Different Temratures.*—As heretofore, a description is given of one experiment rried out at a low temperature and one at a high temperature.

(*a*) Kahlbaum's dibenzylamine (4 g.) was allowed to flow during iours through a capillary tube into 20 c.c. of nitric acid (*d* 1·5) aintained at — 5° to 0°. After keeping for a further hour at e same temperature, the product was poured on to ice and the rstalline precipitate collected and crystallised from 800 c.c. of iling water, when 5·0 g. of pure *mm'*-dinitrodibenzylamine rate separated in clusters of needles, m. p. 235° (decomp.). It s identified by analysis and by direct comparison with a genuine ecimen (below), and also by converting it into the free base, ich was crystallised and similarly identified. The crystals tained on evaporating the mother-liquors (2 g.) obviously conted of a mixture, and, by fractional crystallisation from water, d extraction with small amounts of boiling water, were divided o a less soluble salt, identical with that obtained above, and a re soluble salt, which, when pure, had m. p. 210° and was identid as *pp'*-dinitrodibenzylamine nitrate by analysis and by comrison with a specimen obtained as described below. The yields *pp'*- and *mm'*-dinitro-products isolated were 5% and 80% pectively. A third isomeride appeared to be present, but could be fully purified; it may have been the *mp'*-compound, as it pressed the m. p. of an authentic specimen of the *oo'*-isomeride admixture.

(*b*) On adding dibenzylamine rapidly to 10 parts by weight of ric acid (*d* 1·5) at 70—90°, and pouring the product into water, *a'*-dinitrodibenzylamine nitrate was obtained in almost theoretical ld. No isomeride could be isolated.

oo'-Dinitrodibenzylamine, $(NO_2{\cdot}C_6H_4{\cdot}CH_2)_2NH$.—This substance, pared by Gabriel and Jansen's method (*loc. cit.*), melted at °, and its hydrochloride at 238° (decomp.). Gabriel and Jansen ord the m. p. of the base as 99—100° and that of the hydroloride as "above 220°." Birk gives m. p. 236° for the hydroloride (*J. pr. Chem.*, 1897, **56**, 360).

The *nitrate* separated from water in pale yellow needles, m. p. 0)—203° (decomp.) (Found : C, 47·9; H, 3·9. $C_{14}H_{14}O_7N_4$ quires C, 48·0; H, 4·0%).

mm'-Dinitrodibenzylamine.—A solution of *m*-nitrobenzyl chloride 5 parts of 10% alcoholic ammonia was kept until crystals ceased form, when they were collected, lixiviated with water to remove monium chloride, and crystallised from alcohol or ether, from

which stout, lemon-yellow prisms separated, m. p. 83·5°. further quantity was obtained from the semi-solid mass remaini on evaporation of the ammoniacal alcoholic solution by alternate extracting with water and crystallising from alcohol (Found C, 58·6; H, 4·4. $C_{14}H_{13}O_4N_3$ requires C, 58·5; H, 4·5%).

The *hydrochloride*, formed by dissolving the base in hot dilu hydrochloric acid and cooling, crystallised in small, very pa yellow prisms, m. p. 253°; whilst the *nitrate*, prepared similarl or by nitration as described above, separated in bunches of ve pale yellow needles, m. p. 235° (decomp.) (Found: C, 48·2; H, 4· $C_{14}H_{14}O_7N_4$ requires C, 48·0; H, 4·0%).

pp′-*Dinitrodibenzylamine*.—This was prepared from *p*-nitr benzyl chloride and alcoholic ammonia as in the experime described above. The base separated from alcohol in pale bu needles, m. p. 93° (Found: C, 58·5; H, 4·6%). It is only sparing soluble in ether (distinction from the *mm′*-compound).

The *hydrochloride* crystallises from hot water in clusters of colou less needles, m. p. 217—218°, and the *nitrate*, prepared either nitration of dibenzylamine as described above, or by cooling solution of the dinitro-base in hot dilute nitric acid, forms ve pale yellow leaflets, m. p. 210—211° (decomp.) (Found: C, 48· H, 4·3. $C_{14}H_{14}O_7N_4$ requires C, 48·0; H, 4·0%).

(vii) *Methyldibenzylamine*, $(C_6H_5{\cdot}CH_2)_2NMe$.—Benzyl chlori (20 g.) was dissolved in 200 c.c. of ethyl alcohol and mixed wi 40 c.c. of 33% aqueous methylamine. The reaction was allow to proceed in the cold and finished by heating at 60° for a sho time. After evaporation of the alcohol the bases were extract with ether, after the addition of sodium hydroxide, and treat with *p*-toluenesulphonyl chloride as described on p. 1812. extracting an ethereal solution of the crude product thus obtain with dilute hydrochloric acid a solution of dibenzylamine hydr chloride was obtained; the free base, isolated from this by extra tion with ether after the addition of alkali, had b. p. 290° (uncor (Emde, *Arch. Pharm.*, 1909, **247**, 369, records b. p. 304—30 corr.). The *hydrochloride*, crystallised from a concentrated soluti in hydrochloric acid, has m. p. 200—201° (Found: Cl, 14 $C_{15}H_{18}NCl$ requires Cl, 14·0%).

The nitration of this substance was carried out both in carefu cooled, and in warm, nitric acid, but substantially the same resu were obtained in the two cases, and the following description w suffice as illustration. The base was allowed to flow through fine capillary tube into seven times its weight of 95% nitric a at 0°. The product was allowed to warm to the ordinary te perature during 2 hours and was then mixed with ice, when

ly precipitate was obtained which solidified. This was suspended aqueous sodium hydroxide and shaken with ether, and the hereal solution obtained was dried and evaporated, yielding a lid residue consisting mainly of *pp'*-dinitrodibenzylmethylamine. his substance was readily isolated by crystallisation from alcohol id was identified with an authentic specimen prepared as described elow. The ultimate residues from these crystallisations were oily, it responded to seeding with a crystal of the pure *oo'*-dinitro- mpound, a small amount of which was isolated by draining e adhering oil into porous porcelain and crystallised from her. It was identified by direct comparison and a mixed m. p. termination.

oo'-Dinitrodibenzylmethylamine, $(NO_2 \cdot C_6H_4 \cdot CH_2)_2N \cdot CH_3$.—A mixre of *o*-nitrobenzyl chloride (5 g.), absolute alcohol (30 c.c.), and % aqueous methylamine (15 c.c.) was kept at the ordinary mperature for a week. The crystals which had separated were crystallised from alcohol, when stout, yellow prisms were obtained greeing in their m. p. (63°) and properties with the description of '-dinitrodibenzylmethylamine given by Gabriel and Jansen (*loc.* .).

The *hydrochloride* crystallised from dilute hydrochloric acid in lourless needles, m. p. 216° (Found: Cl, 10·3. $C_{15}H_{16}O_4N_3Cl$ quires Cl, 10·5%), and the *nitrate* from dilute nitric acid in very le yellow prisms, m. p. 125° (decomp.).

mm'-Dinitrodibenzylmethylamine, prepared in like manner from -nitrobenzyl chloride and methylamine, separated from ethyl cohol in colourless needles, m. p. 83—84° (Found: C, 59·9; , 5·1. $C_{15}H_{15}O_4N_3$ requires C, 60·0; H, 5·0%).

The *hydrochloride*, prepared by evaporating a solution of the se in hydrochloric acid and crystallising the residue from alcohol, rmed pale buff prisms, m. p. 223—224° (Found: Cl, 10·2. $_5H_{16}O_4N_3Cl$ requires Cl, 10·5%), and the *nitrate*, crystallised m dilute nitric acid, was obtained as small, pale yellow prisms, p. 163° (decomp.).

pp'-Dinitrobenzylmethylamine.—This was obtained by the same thod and had the m. p. and properties recorded by Paal and renger (*Ber.*, 1897, **30**, 63).

The *hydrochloride*, prepared as in the previous case, crystallised m ethyl alcohol in stout, pale yellow prisms, m. p. 204—205° ound: Cl, 10·4%), whilst the *nitrate*, after twice crystallising m water, formed pale yellow prisms, m. p. 146° (Found: C, 49·3; 4·7. $C_{15}H_{16}O_7N_4$ requires C, 49·4; H, 4·4%).

(viii) *Acetobenzylamide*, $C_6H_5 \cdot CH_2 \cdot NH \cdot CO \cdot CH_3$.—The nitration this substance has been described by Amsel and Hofmann (*loc.*

cit.), who obtained aceto-*p*-nitrobenzylamide; but they do not mention any by-products. Having repeated the experiment, utilising our experience in the separation of the acetyl derivatives of *o*-, *p*-, and *m*-nitrobenzylamines, we have come to the conclusion that, although aceto-*o*- or -*m*-nitrobenzylamide (or both) is probably formed along with the *p*-compound, the quantity must be very small, for it could not be identified with certainty. This is in agreement with the rather strongly basic character of acetobenzylamide.

(ix) *Acetomethylbenzylamide*, $C_6H_5 \cdot CH_2 \cdot NMe \cdot CO \cdot CH_3$.—This substance was prepared by boiling methylbenzylamine with 2·5 parts of acetic anhydride for 15 minutes, and then boiling the product for a few minutes with excess of water. The oil, extracted with ether after the addition of excess of sodium hydroxide, gradually solidified on keeping in an evacuated desiccator and could then be crystallised from ether–ligroin (b. p. 40—60°), from which it separated in large, colourless cubes, m. p. 41—43°, b. p. 155°/16 mm. (Found: C, 73·3; H, 7·9. $C_{10}H_{13}ON$ requires C, 73·6; H, 8·0%). The same substance was obtained as a by-product in the preparation of dibenzylmethylamine described above. It is completely soluble in cold 3% hydrochloric acid.

The nitration was carried out by adding the substance in small portions to 10 parts of nitric acid (*d* 1·5) at $-10°$. The liquid was allowed to warm during 1 hour to the ordinary temperature, and was then mixed with ice. No precipitation took place under this treatment, and the solution was therefore rendered alkaline and extracted with ether, when, on evaporation of the solvent, a solid residue was obtained which crystallised from ligroin in clusters of colourless needles, m. p. 80—81°. The substance also separated from alcohol–ligroin in stout prisms of the same m. p. It was identified as aceto-*p*-nitrobenzylmethylamide by analysis and by comparison with a synthetic specimen (below). The mother-liquors were carefully searched for an isomeride, but although a further quantity of the *p*-nitro-compound was obtained (total yield 90%), the *o*- and *m*-nitro-isomerides could not be identified with certainty, although traces of a more fusible compound were present.

Aceto-o-*nitrobenzylmethylamide*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NMe \cdot CO \cdot CH_3$, was prepared by Gabriel and Jansen's method.

Aceto-m-*nitrobenzylmethylamide* was prepared from the hydrochloride of *m*-nitrobenzylamine by boiling it (1 g.) for 15 minutes with acetic anhydride (4 c.c.) and anhydrous sodium acetate (1 g.). The product was warmed with water to decompose the excess of acetic anhydride, and the solution made alkaline and extracted with ether, from which, on evaporation, an oily residue was obtained

which quickly solidified, and, on crystallisation from benzene–ligroin, yielded colourless prisms, m. p. 56—57° (Found: C, 57·5; H, 5·9. $C_{10}H_{12}O_3N_2$ requires C, 57·7; H, 5·8%).

Aceto-p-*nitrobenzylmethylamide*, prepared similarly, separated from benzene–ligroin in colourless prisms, m. p. 80—81° (Found: C, 57·6; H, 6·0%).

(x) *Acetodibenzylamide*, $(C_6H_5\cdot CH_2)_2N\cdot CO\cdot CH_3$.—This substance was prepared by boiling dibenzylamine for a few minutes with acetic anhydride and decomposing the excess of the reagent with water. It was extracted from alkaline solution by means of ether, and, after distillation, was obtained as a rather viscous oil, b. p. 194—195°/3 mm. (Found: C, 79·9; H, 7·0. $C_{16}H_{17}ON$ requires C, 80·0; H, 7·1%). It was also prepared by treating a pyridine solution of dibenzylamine with acetyl chloride and extracting with ether after adding excess of dilute hydrochloric acid. It is easily soluble in concentrated hydrochloric acid, but only sparingly soluble in dilute acid. On boiling for 6 hours with 20% hydrochloric acid, hydrolysis of the acetyl group took place, and the solution on cooling deposited crystals of dibenzylamine hydrochloride.

Nitration with Different Concentrations of Nitric Acid.—(*a*) The acetyl compound (2·5 g.) was added in about 15 portions during 1½ hours to 15 g. of 95% nitric acid at about − 5°. At each addition a deep red colour was formed which vanished after a few seconds. The product was kept for a further hour at 0°, and at the ordinary temperature for the same period, and then mixed with ice. The oily precipitate slowly solidified and after crystallising from alcohol yielded 1·5 g. of crystals, m. p. 175°. After complete purification, these had m. p. 183° and were identified as aceto-*pp'*-dinitrodibenzylamide by direct comparison with a specimen of this substance, and by converting them by hydrolysis (boiling for 6 hours with 20% hydrochloric acid) into *pp'*-dinitrodibenzylamine which, along with its hydrochloride, was similarly identified. The alcoholic mother-liquors were evaporated and the residue was fractionally crystallised from alcohol, when aceto-*mm'*-dinitrodibenzylamide was readily isolated in a pure condition and identified by direct comparison with an authentic specimen (below). The ultimate residues yielded (besides a further quantity of the *pp'*-compound) a very small amount of the *oo'*-isomeride, which was obtained from gummy residues by seeding with a pure specimen. The quantities isolated were: *para* 45%; *meta* 20%; *ortho* 3%.

(*b*) The dibenzylamide was treated at 30—50° with 80% nitric acid, and the product isolated and separated as described above. Yields: *para* 30%; *meta* 40%; *ortho* trace.

(*c*) The dibenzylamide was boiled with 70% nitric acid for 15

minutes, and the products were isolated and separated. Yields *para* 20%; *meta* 55%.

Aceto-oo′-dinitrodibenzylamide, $(NO_2 \cdot C_6H_4 \cdot CH_2)_2N \cdot CO \cdot CH_3$, was prepared from the corresponding base by acetylation with boiling acetic anhydride. After decomposing the acetic anhydride by boiling with water, sufficient additional acetic acid was added to complete the solution of the acetyl compound. On cooling, clusters of very pale yellow needles separated, m. p. 154° (Found: C, 58·6; H, 4·4. $C_{14}H_{15}O_5N_3$ requires C, 58·4; H, 4·5%).

Aceto-mm′-dinitrodibenzylamide, prepared in exactly the same way, crystallised in small, pale yellow prisms, m. p. 146° (Found: C, 58·5; H, 4·5%).

Aceto-pp′-dinitrodibenzylamide, obtained likewise, separated in colourless needles, m. p. 183—184° (Found: C, 58·3; H, 4·5%).

(xi) *Diacetylbenzylamine*, $C_6H_5 \cdot CH_2 \cdot N(CO \cdot CH_3)_2$.—Benzylamine (5 g.) was boiled with acetic anhydride (20 c.c.) for 3 days, after which the solution was cooled and shaken with water until the excess of acetic anhydride had decomposed. The solution was then made alkaline and extracted with ether. The residue from the ether evidently consisted of a mixture of mono- and di-acetyl derivatives, since some of the former compound crystallised on keeping for a few days in an evacuated desiccator. To isolate the diacetyl compound the mixture was dissolved in ether and the monoacetyl derivative removed by shaking with 5% hydrochloric acid. On evaporation of the ether an oil was obtained which refused to solidify and was therefore purified by distillation. Di-acetylbenzylamine is a colourless, rather viscous liquid, b. p. 176—178°/30 mm. (Found: C, 69·1; H, 7·2. $C_{11}H_{13}O_2N$ requires C, 69·2; H, 6·9%). It is completely hydrolysed to benzylamine hydrochloride on boiling for 16 hours with 20% hydrochloric acid.

The substance was allowed to flow through a fine capillary tube into 10 parts of 95% nitric acid at — 20°, and the resulting solution mixed with crushed ice. The oily product thus obtained was extracted with ether after the addition of sodium hydroxide, and as it did not solidify after evaporation of the ether, was hydrolysed by boiling for 12 hours with 20% hydrochloric acid. On evaporating the solution so obtained, a solid residue remained, consisting of *m*-nitrobenzylamine hydrochloride, which was readily isolated in the pure condition by crystallisation from alcohol, and identified by direct comparison with a genuine specimen. No by-product could be recognised.

Some of the analyses recorded in this paper were carried out by Mr. Arthur Rumfit, to whom the authors acknowledge their

ndebtedness. They also desire to record their thanks to the Chemical Society for a grant wherewith part of the expense of this esearch has been defrayed.

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CCXLI.—*Syntheses of Disulphoxides.*

By DAVID TEMPLETON GIBSON, CECIL JAMES MILLER, and SAMUEL SMILES.

FOUR general methods of obtaining the disulphoxides are at present available, but the very simple synthesis from a mercaptan and a sulphonyl chloride, although frequently attempted, has not yet been successfully accomplished. Blomstrand (*Ber.*, 1870, **3**, 962)

$$(a)\ RSO_2Cl + R'SH = HCl + RSO_2{\cdot}SR'$$

claimed to have obtained tolyl amyl disulphoxide from amyl mercaptan and toluenesulphonyl chloride, but his product was ill-defined and apparently not analysed; thus Otto, after further investigation of the reaction, was fully justified in doubting this result (*Ber.*, 1882, **15**, 121). Otto also attempted to obtain diphenyl and ditolyl disulphoxides (*Ber.*, 1876, **9**, 1636; 1878, **11**, 2070) by this method, but was unsuccessful, isolating instead the corresponding disulphide and sulphinic acid. He represented the completed reaction as follows:

$$(b)\ RSO_2Cl + 2RSH = HCl + RSO_2H + (RS)_2.$$

Many other observers have since met with Otto's experience and agree with his representation of the process.

The circumstance that the disulphoxides apparently cannot be obtained in this manner has been utilised by Hinsberg (*Ber.*, 1903, 36, 109) and by Fromm and Seixas Palma (*Ber.*, 1906, **39**, 3310) as evidence against the thiolsulphonate structure of these substances. Conclusive evidence in favour of this constitution has been obtained (J., 1924, **125**, 176; this vol., p. 224). Hence it seemed necessary to find an explanation of this discrepancy, and a further examination of the reaction between mercaptans and sulphonyl halides has now been made. In the reaction between disulphoxides and mercaptans the former undergo fission, yielding a sulphinic acid whilst the thioaryl group appears as disulphide (*loc. cit.*):

$$(c)\ RSO_2SR' + R'SH = RSO_2H + (R'S)_2.$$

Since this decomposition of the disulphoxides takes place very easily, it seemed probable that the reaction between sulphonyl halide and mercaptan may proceed in two stages, the disulphoxide

at first formed (according to *a*) being rapidly decomposed (compar *c*) by the mercaptan. According to this hypothesis it should b possible to obtain disulphoxides by the method if experimenta conditions are adopted in favour of (*a*) and unfavourable to (*c* In one set of experiments these have been attained by slowly addin the mercaptan to a large excess of the heated sulphonyl chloride thus completing (*a*) as rapidly as possible and avoiding the exces of mercaptan necessary to (*c*). In other experiments the mor reactive sulphonyl iodides were used, the secondary action of th mercaptan being to a great extent avoided by the use of silve mercaptides. With these modified conditions the method ma be used for the synthesis of disulphoxides and, as shown below the somewhat inaccessible class of disulphoxides containing dis similar aromatic nuclei are readily obtained. Of the two method described, that involving the use of the sulphonyl iodides is usuall to be preferred, but owing to the tendency of these substances t liberate iodine some disulphide may be formed from the mercaptide The success of this method is therefore more easily attained b using the more stable of the sulphonyl iodides and by choosin mercaptans which generate the soluble disulphides. The latte condition facilitates separation of the impurity from the required disulphoxide.

It is now evident that the failure to obtain disulphoxides from these reagents under ordinary conditions can no longer be used as objection to the thiolsulphonate structure; on the contrary, the results now described give further evidence in support of this.

Experimental.

(a) *Syntheses from Mercaptans and Sulphonyl Chlorides.*—The conditions adopted were as follows. A solution of the mercaptan in benzene containing a small quantity of pyridine was slowly added to a boiling solution of excess of the sulphonyl chloride in the same solvent. When the liquid had cooled, any sulphinic acid pyridine, and the excess of acid chloride present were removed The solvent was evaporated and the residue was examined.

Di-*p*-tolyl disulphoxide was obtained in 25% yield from 2 mols of the mercaptan and 5 mols. of *p*-toluenesulphonyl chloride. It was isolated and identified in the usual manner.

2 : 5 : 2′ : 5′-Tetrachlorodiphenyl disulphoxide was obtained (5% yield) from 2 : 5-dichlorothiophenol (1 mol.) and 2 : 5-dichlorobenz enesulphonyl chloride (7 mols.). The product (m. p. 127°) was identified in the usual manner.

4-*Tolyl* 3-*nitrobenzenethiolsulphonate*, $C_6H_4Me{\cdot}S{\cdot}SO_2{\cdot}C_6H_4{\cdot}NO_2$ was isolated (30% yield) from the reaction between 3-nitrobenzene

sulphonyl chloride (8 mols.) and 4-tolyl mercaptan (1 mol.). The substance, isolated as usual, formed colourless needles, m. p. 109° (Found: C, 50·4; H, 3·6; N, 4·9. $C_{13}H_{11}O_4NS_2$ requires C, 50·5; H, 3·5; N, 4·5%).

The ascribed constitution was confirmed by treating the substance in warm alcohol with 2 : 5-dichlorothiophenol (1 mol.). 3-Nitrobenzenesulphinic acid and 2 : 5-dichloro-4′-methyldiphenyl disulphide were isolated (J., 1924, **125**, 182).

(b) *Syntheses from Sulphonyl Iodides and Silver Mercaptides.*—The sulphonyl iodides (Otto and Tröger, *Ber.*, 1891, **24**, 478) were prepared by slowly adding an alcoholic solution of the theoretical amount of iodine to a cold solution of the sodium sulphinate containing about 20 g. of the salt in 2—3 litres of water. The crystalline material was washed and dried (yield, under the best conditions, generally over 80%).

2 : 5-*Dichlorobenzenesulphonyl iodide*, $C_6H_3Cl_2{\cdot}SO_2I$, separated from light petroleum in golden-yellow needles, m. p. 100° (Found: Cl + I, 58·7; S, 9·35. $C_6H_3O_2Cl_2IS$ requires Cl + I, 58·7; S, 9·6%).

Naphthalene-2-sulphonyl iodide, $C_{10}H_7{\cdot}SO_2I$, separated from benzene–light petroleum in yellow needles, m. p. 96—97° (decomp.). This sulphonyl iodide was more stable in solution than any other encountered in these experiments (Found: I, 40·0; S, 10·0. $C_{10}H_7O_2IS$ requires I, 39·9; S, 10·0%).

The silver mercaptides used were obtained from silver nitrate, the mercaptan, and sodium acetate (1 mol.) in alcoholic solution.

The dry silver mercaptide (rather more than 1 mol.) was gradually added with thorough shaking to a dry solution of the sulphonyl iodide in ether or benzene. Owing to the tendency of solutions of the iodides spontaneously to liberate iodine, the duration of the process was kept within certain limits—generally about ½ hour—which varied with different sulphonyl iodides. The silver halide was then removed and the solution was treated with a little dilute aqueous sodium carbonate and, if necessary, with sufficient sodium sulphite to remove free iodine. After the solvent had been removed the residue was purified in the usual manner. In this way the following thiolsulphonates were obtained.

2 : 5-Dibromophenyl 2 : 5-dichlorobenzenethiolsulphonate,

$$C_6H_3Br_2{\cdot}S{\cdot}SO_2{\cdot}C_6H_3Cl_2,$$

from 2 : 5-dichlorobenzenesulphonyl iodide and 2 : 5-dibromophenyl mercaptan (88% yield). The product (m. p. 124°) was identified with that obtained from silver dichlorobenzenesulphinate and dibromophenylsulphur bromide (this vol., p. 230) (Found: S, 13·3. Calc., S, 13·4%).

4-*Tolyl* 2 : 5-*dichlorobenzenethiolsulphonate*, $C_6H_4Me{\cdot}S{\cdot}SO_2{\cdot}C_6H_3Cl_2$, was obtained (80% yield) from 2 : 5-dichlorobenzenesulphonyl iodide and silver 4-tolyl mercaptide. The subtance separated from aqueous alcohol in small, colourless needles, m. p. 74° (Found: S, 19·2; Cl, 21·4. $C_{13}H_{10}O_2Cl_2S_2$ requires S, 19·25; Cl, 21·2%).

6-*Methoxy*-3-*tolyl* 2-*naphthalenethiolsulphonate*, $OMe{\cdot}C_6H_3Me{\cdot}S{\cdot}SO_2{\cdot}C_{10}H_7$, was prepared (about 85% yield) from 2-naphthalenesulphonyl iodide and 4-methoxytoluene 3-mercaptan (J., 1923, **123**, 2390). After purification from hot alcohol the substance formed colourless prisms, m. p. 113—114° (Found: C, 62·6; H, 4·7; S, 18·5. $C_{18}H_{16}O_3S_2$ requires C, 62·7; H, 4·6; S, 18·6%).

2 : 4-*Xylyl* 2-*naphthalenethiolsulphonate*, $C_6H_3Me_2{\cdot}S{\cdot}SO_2{\cdot}C_{10}H_7$, was obtained (about 85% yield) from 2-naphthalenesulphonyl iodide and 2 : 4-xylylthiol. It separated from benzene–ligroin in colourless prisms, m. p. 80—81° (Found: C, 65·5; H, 4·9; S, 19·2. $C_{18}H_{16}O_2S_2$ requires C, 65·8; H, 4·9; S, 19·5%).

We are indebted to the Chemical Society for a grant which partly defrayed the cost of these experiments.

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CCXLII.—*Studies of Electrolytic Polarisation. Part III. The Diffusion Layer.*

By SAMUEL GLASSTONE.

SINCE Noyes and Whitney (*Z. physikal. Chem.*, 1897, **23**, 689) first put forward the view that diffusion plays the chief part in the rate of a heterogeneous process such as solution, and Nernst *et al.* (*ibid.*, 1904, **47**, 52; 1905, **53**, 235) extended the idea to chemical and electrochemical reactions in heterogeneous systems, most authors have accepted the idea of the existence of a layer of liquid of different concentration from that of the bulk of the solution at the surface of the reacting solid or the electrode in the case of an electrolytic process. The thickness of this layer has been presumed to be independent of the concentration of the liquid, and even to vary only slightly with the nature of the two phases involved in the reaction. Further, in the case of electrolytic reduction Jahn ("Grundriss der Elektrochemie," 1905, p. 519 *et seq.*) quotes results from the work of Haber *et al.* (*Z. physikal. Chem.*, 1900, **32**, 193, 271; 1904, **47**, 257) and from that of Akerberg (*Z. anorg. Chem.*,

902, **31**, 161) which indicate that the thickness of the diffusion ayer for a given electrode and electrolyte is also independent of he current density under such conditions that very little or no gas s being evolved. The results obtained by Nernst and Merriam *Z. physikal. Chem.*, 1905, **53**, 235) and by Wilson and Youtz *J. Ind. Eng. Chem.*, 1923, **15**, 603), as well as unpublished measure- nents by the present author, all lead to the same conclusion. When a heterogeneous reaction involves the liberation of gas, as in he dissolution of metals in acid, the results of Palmaer (*Z. physikal. Chem.*, 1906, **56**, 689) and of Prins (*Proc. K. Akad. Wetensch. Amsterdam*, 1921, **23**, 1449) indicate that it is very probable that he thickness of the diffusion layer does not remain constant; no work, however, appears to have been done in connexion with the iffusion layer in an electrolytic process involving free evolution of as, but the results described below have an important bearing on his problem. These results were obtained in the course of experi- nents on lead and mercury cathodes in various electrolytes, some f the results of which have already been published (J., 1924, **125**, 414, 2646). An examination of the figures given in these papers vill show that under a variety of conditions the difference between he direct and the extrapolated overvoltage, which is presumably lue to the resistance at the electrode surface, is not nearly pro- ortional to the magnitude of the current. This indicates that the alue of the resistance alters with the current as long as gas bubbles re being evolved; actually the resistance decreases as the current s increased. A large part of this resistance is believed to be due o the presence of a thin layer of dilute electrolyte—the diffusion ayer—which is in immediate contact with the electrode; it thus ppears that the resistance, and probably the thickness, of this ayer decreases as the current density is increased. This is no loubt due to the fact that the rapid evolution of gas at the high urrent densities causes a stirring of the electrolyte which results n a reduction of the thickness of the diffusion layer. Further onfirmation of this view has been obtained by experiments with a nercury cathode in dilute solutions of sulphuric acid containing otassium sulphate, and with various electrodes in hydrochloric cid solution.

The experimental results have thrown further light on the factors nfluencing the rate of fall of the back *E.M.F.* of a polarised elec- rode; in the previous work on the mercury cathode (*loc. cit.*) it vas shown that the diffusion of oxygen from the anode can affect he back *E.M.F.* and it is now found that the thickness of the liffusion layer may also influence the rate of fall.

Experimental.

The apparatus used in this work was the same as that describe in previous communications (*loc. cit.*); unless otherwise stated, th experiments were carried out at room temperature (about 15°) an anode and cathode compartments were not separated.

Sulphuric Acid and Potassium Sulphate Solutions.—During th course of the measurements of the overvoltage at the mercur cathode in *N*/16-sulphuric acid containing potassium sulphate (se J., 1924, **125**, 2651) it was found that, although the back *E.M.F* of the electrode decreased normally for the first 0·012 sec. afte the polarising current was switched off, yet in certain cases, afte this period had elapsed, an abnormal condition set in which wa independent of the nature of the electrode vessel, and of the separ ation or not of the anode and cathode compartments. The followin typical result will make this abnormality clear:

Back *E.M.F.* after:	C.D. (amp./cm.²)	0·003	0·006	0·012	0·024
0·012 sec.		0·91	0·92	0·92	0·92
0·018 „		0·89	0·89	0·85	0·85

After a certain interval of time, instead of the normal decrease o the back *E.M.F.* there was a sudden, more rapid, fall of potentia This fall was first observed at the highest current densities used but after increasing time intervals it was found to occur at lowe current densities. At a higher temperature the sudden fall o potential took place after a shorter interval of time for any par ticular current density. This curious behaviour was noted in al cases where the electrolyte contained an excess of potassium ion and where the potentials indicated that the normal hydroge discharge was not the only cathodic process. Similar experiment in which sodium sulphate was used instead of the potassium sal gave similar results.

The potential measurements suggest that the hydrogen-ion con centration in the vicinity of the electrode in these solutions i impoverished, probably owing to the fact that the presence of a large excess of potassium ions prevents the hydrogen ions fron diffusing up to the electrode as fast as they are discharged; the potential of the electrode becomes more negative and potassium ions are discharged to form an amalgam. When the polarising current is switched off, the hydrogen ions can diffuse through the impoverished layer of electrolyte without being discharged and s react with the amalgam, causing its rapid decomposition (see Klein *Z. anorg. Chem.*, 1924, **137**, 39) and a consequent fall of potential the thinner the diffusion layer the sooner will this sudden fall o potential occur. The results given above show that this fall occurs

ponest at the highest current densities, and hence we may conclude hat under conditions of gas evolution the diffusion layer is thinnest t high current densities. An increase of temperature causes the ate of diffusion to increase, even if it does not appreciably influence he thickness of the diffusion layer, and so the time interval between witching off the current and the sudden fall of back *E.M.F.* is iminished. These conclusions regarding the diffusion layer in the pecial case under discussion are in agreement with those arrived t from a consideration of the difference between the direct and ic extrapolated overvoltage measurements.

If the above views are correct it is to be expected that rapid irring of the electrode and electrolyte will have some influence on ie fall of the back *E.M.F.* In these circumstances the diffusion ayer would cease to exist the instant that the polarising current as switched off, and so a more rapid fall of potential right from ie beginning would be expected at all current densities, but no idden fall after an interval of time. These forecasts have been onfirmed; up to 0·03 sec. after the polarising circuit was broken ie rate of fall of the back *E.M.F.* was still normal at all the current ensities used in the previous experiments; this rate of fall was reater initially than in a similar experiment in which the electrolyte as not stirred. The following figures illustrate the effect of irring.

Back *E.M.F.* after :	C.D. amp./cm.^{2}	0·002	0·004	0·008	0·016	
0·002 sec.		0·98	1·00	1·02	1·04	
0·006 ,,		0·95	0·97	0·99	1·01	Not stirred.
0·018 ,,		0·88	0·90	0·91	0·89	
0·002 ,,		0·92	0·94	0·96	0·99	
0·006 ,,		0·87	0·89	0·91	0·94	Stirred.
0·018 ,,		0·81	0·83	0·85	0·87	

Hydrochloric Acid Solutions.—In the course of experiments with -hydrochloric acid as electrolyte, chlorine gas was always evolved the anode. If the anode and cathode compartments were parated, no special precautions were taken before making measure-ents; in other cases the polarising current was passed for some me so that the electrolyte dissolved a considerable amount of ilorine gas. In the latter circumstances no hydrogen could be erated at the cathode unless a high current density was applied, ., 0·24 amp. per 10 sq. cm., but once gas evolution had commenced ie current could be reduced by gradual stages to 0·015 amp. and ie evolution of gas would continue. If the current was reduced ddenly, gas evolution ceased. In making measurements it was ual to determine the potential by the direct method first, and en to measure the back *E.M.F.* at certain definite times after the

polarising current was switched off, first with decreasing and the with increasing current densities. The results quoted below a the mean of those obtained with increasing and decreasing current the actual values for the same current density did not va appreciably.

The following table contains the results obtained with a mercu cathode of 10 sq. cm. exposed area in N-hydrochloric acid; t anode and cathode compartments were not separated.

C.D.	Overvoltage.		Back $E.M.F.$ after :						
(amp./cm.^{2}).	Direct.	Extrap.	0·002	0·004	0·006	0·008	0·012	0·018	sec.
0·0015	1·03	1·01	0·98	0·96	0·94	0·91	0·89	0·84	
0·003	1·07	1·03	1·00	0·98	0·96	0·91	0·89	0·84	
0·006	1·11	—	0·99	0·97	0·95	0·89	0·84	*0·74	
0·012	1·15	—	0·97	0·94	0·89	0·80	*0·67	0·50	
0·024	1·19	—	0·93	0·89	0·83	*0·67	0·49	0·28	

These results show that there are two distinct abnormalities i the fall of the back $E.M.F.$ after the polarising current is switche off. In the first place, although the direct overvoltage increas regularly, yet the back $E.M.F.$ after 0·002 sec. at first increas and then decreases as the current density is increased. Th suggests that immediately the current is switched off at the hig current densities there is a very rapid fall of potential which cann be detected directly. Following this the rate of fall of potenti is fairly regular until after a certain interval of time there is anoth sudden fall in the back $E.M.F.$ at the points marked with a asterisk in the above table. The period of time that elapses befo this second fall of potential occurs decreases as the current densit is increased. This fall of potential is not due to the failure of th electrode to reach its equilibrium condition when the current switched on, since measurements have shown that at these hig current densities almost the same potential is reached while th current is flowing whether the commutator is working or not.

In the next experiments the anode and cathode compartment were separated by placing the mercury in a porous pot; the platinu anode was placed in the liquid which surrounded the pot. Th same electrolyte, N-hydrochloric acid, was used throughout. Th results were as follows.

C.D.	Overvoltage.		Back $E.M.F.$ after			
(amp./cm.^{2}).	Direct.	Extrap.	0·002	0·004	0·006	0·012 sec.
0·0015	1·03	1·01	0·98	0·96	0·94	0·89
0·003	1·07	1·03	0·99	0·97	0·95	0·89
0·006	1·11	1·04	1·00	0·98	0·96	0·90
0·012	1·15	1·05	1·01	0·99	0·97	0·91
0·024	1·19	1·06	1·02	0·99	0·97	0·91

These figures appear to be quite normal in every way, and hen it may be concluded that the abnormal fall of the back $E.M.$

bserved in the previous experiment is due to the action of the hlorine gas liberated at the anode; in all cases where the chlorine as prevented from diffusing to the cathode the fall of potential as normal, but in other cases it was abnormal. In order to etermine the influence, if any, of the material of the electrode essel on the abnormal results, the platinum anode was placed inside he porous pot containing the mercury; the potentials were almost he same as those obtained with the mercury in a glass beaker, nd hence the experiment did not yield any decisive result. Using glass beaker which had been standing with concentrated alkali or about a week, the following back *E.M.F.*'s were measured at ·002 sec. after the polarising current was switched off :—

C.D.	0·0015	0·003	0·006	0·012	0·024
Back *E.M.F.*	0·96	0·97	0·95	0·91	0·80

The inside of the beaker was then coated with paraffin wax and he following measurements were then recorded at the same series f current densities :—

Back *E.M.F.*	0·96	0·97	0·98	0·97	0·95

The initial fall in the back *E.M.F.* at high current densities is thus nfluenced to some extent by the material of the electrode vessel, nd different results were obtained from time to time with different glass beakers. The sudden fall that occurred after the lapse of an nterval of time was always observed, provided the anode and athode compartments were not separated.

Discussion.

Applying the suggestions that have been put forward to explain he abnormal back *E.M.F.* of the mercury cathode in dilute ulphuric acid solutions (see Part II, *loc. cit.*), it appears that the irst rapid fall of potential at the high current densities is to be ttributed to the concentration of the electromotively active material t the circumference of the electrode owing to the action of surface ension forces. As soon as the polarising current is switched off his active substance appears to be rapidly attacked by the chlorine n solution, and the material of the electrode vessel may influence he rate of reaction; there is thus a rapid initial fall of potential. f the mercury was in such a condition that the surface forces were o longer operative, then this rapid fall of potential should not be bserved; some experiments were therefore made with an amal- amated lead electrode, which in most cases gives overvoltages hat are not very different from those given by pure mercury. The electrodes used had an exposed area of 7·5 sq. cm. and the irect overvoltages were almost the same as those observed with a

pure mercury surface of the same area. The back *E.M.F.* measured at 0·002 sec. after the polarising current was switched off increased regularly as the current density increased independently of whether the anode and cathode compartments were separated or not, and showed no signs of abnormality.

C.D. (amp./cm.²)	0·004	0·008	0·016	0·032
Direct overvoltage	1·07	1·11	1·15	1·18
Back *E.M.F.* after 0·002 sec.	0·87	0·88	0·90	0·93

The subsequent rate of fall of the back *E.M.F.* was too great to make extrapolation possible, and so the actual overvoltages can only be inferred from the direct measurements. The decrease of back *E.M.F.*, although rapid, was quite regular in those cases in which the anode and cathode compartments were separated, but when this was not the case a sudden fall of potential was observed after an interval of time had elapsed; first at the higher current densities, and after increasing periods at the lower current densities. It appears therefore that the initial sudden fall of potential observed with the mercury cathode in the presence of dissolved chlorine is connected with the surface tension forces that are operative when the current is flowing, but the subsequent rapid fall after an interval of time is due to another cause.

According to the views expressed in connexion with the abnormal results obtained with the mercury cathode in sulphuric acid containing potassium sulphate, the sudden fall of potential that is observed some time after the polarising current is switched off is apparently due to the diffusion of chlorine through the layer of electrolyte in immediate contact with the electrode. Judging by the difference between the direct and the extrapolated overvoltages this layer should be thinnest at the highest current densities, and consequently under these conditions chlorine will take the least time to diffuse through. By removing the active hydrogen very rapidly, the chlorine causes a sudden fall of potential, which will occur soonest at the high current densities; the two tables given above show that the time which elapses between switching off the current and the commencement of this rapid fall of potential is roughly proportional to the resistance which is the cause of the difference between the direct and the extrapolated overvoltages. Since this rapid fall of potential could not be connected in any way with the material of the electrode or of the cell, but should depend simply on the existence of a diffusion layer, it should occur with other electrodes in hydrochloric acid. Experiments with lead and copper electrodes have shown that this is actually the case, although neither of them showed the very rapid initial fall of the back *E.M.F.* that occurred with the mercury cathode, yet in both

ases there was a sudden fall of potential after a certain interval f time; this interval was shortest at the highest current densities. Where the anode and cathode compartments were separated before he electrolyte had dissolved any chlorine gas this rapid fall of potential was not observed in any case investigated hitherto.

Since both types of abnormal back *E.M.F.* are connected in ome way with the chlorine gas dissolved in the electrolyte, but in ne case the fall takes place almost the instant the current is witched off, whilst in the other only after an appreciable interval f time, it is clear that in the former case the diffusion layer must e extremely thin. This means that the layer of solution containing dissolved chlorine must be almost in direct contact with he mercury at its circumference, since it is considered that it is here that the first rapid removal of active material occurs immediately the current is switched off. It is possible that the forces cting at the electrode–electrolyte interface under the influence of he current cause fresh electrolyte containing dissolved chlorine to e drawn continuously towards the circumference of the electrode, nd so no appreciable time elapses for the chlorine to diffuse in. When the current is off, the surface forces are no longer operative, nd so fresh electrolyte is no longer drawn to the circumference of he mercury, neither is there such a large concentration of active aterial in this vicinity; hence the subsequent fall of potential s not very rapid until chlorine diffuses up to the main portion of he electrode surface.

Summary.

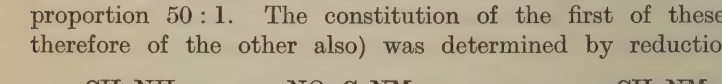
An examination of the difference between the direct and the xtrapolated overvoltages at lead and mercury cathodes in various lectrolytes has led to the conclusion that the thickness of the iffusion layer at an electrode from which gas is being liberated eely decreases as the current density is increased; this is probably ue to the stirring caused by the rapid evolution of bubbles. This iew has been confirmed by an analysis of the abnormal fall in the ack *E.M.F.* of a mercury cathode in a dilute solution of sulphuric cid containing an excess of alkali sulphate, and of various cathodes n *N*-hydrochloric acid saturated with chlorine. In previous work has been found that oxygen diffusing from the anode may influence he initial fall of the back *E.M.F.* of a mercury cathode in a manner hich depends on the material of the electrode vessel and the urrent density; a similar abnormality has been observed as the sult of the diffusion of anodic chlorine towards a mercury cathode n hydrochloric acid solution.

University College, Exeter. [*Received, May 16th*, 1925.]

CCXLIII.—*The* 4- *and* 5-*Nitro*-1 : 2-*Dimethylglyoxaline*

By Vinayak Keshav Bhagwat and Frank Lee Pyman.

In the methylation of 4(5)-nitroglyoxaline (Hazeldine, Pyman, a Winchester, J., 1924, **125**, 1431) and 4(5)-nitro-5(4)-meth glyoxaline (Pyman, J., 1922, **121**, 2616) by methyl sulphate, 3 and 233 times respectively as much of the isomerides wi NO_2 : (*N*)Me in the 5 : 1-positions were isolated as of those wi NO_2 : (*N*)Me in the 4 : 1-positions. Under similar conditio 4(5)-nitro-2-methylglyoxaline (I) yields 5-*nitro*-1 : 2-*dimethylg oxaline* (II) and 4-*nitro*-1 : 2-*dimethylglyoxaline* (III) in the relati proportion 50 : 1. The constitution of the first of these (a therefore of the other also) was determined by reduction a



(I.) (II.) (III.)

fission, as in the investigations cited above, when ammonia, meth amine, and glycine were identified, but here a small quantity of unidentified base, $C_5H_{10}N_2$, was also obtained. On nitrati 1 : 2-dimethylglyoxaline, the 4- and 5-nitro-derivatives w isolated in the relative proportion 2 : 1, this result being similar that obtained by the nitration of 1-methylglyoxaline (Hazeldi Pyman, and Winchester, *loc. cit.*). The 5-nitro-compound gave picrate and is thus a stronger base than the 4-isomeride, from wh no picrate could be prepared. Moreover, the 5-isomeride combi with methyl iodide at 100°, whereas the 4-isomeride does not re with methyl iodide at 100°, although it does so at 150°. T methiodides of the two isomerides are identical, being 4(5)-nit 1 : 2 : 3-trimethylglyoxalinium iodide, which yields on distillat 4-nitro-1 : 2-dimethylglyoxaline. The properties of the isomeri are thus generally similar to those of the 5- and 4-nitro-1-meth glyoxalines.*

The reactivity of the 2-methyl group in these compounds b been examined. Since the bromine atom in 2-bromo-5-nit 1 : 4-dimethylglyoxaline can be replaced by the sulphonic a residue (Pyman and Timmis, J., 1923, **123**, 494), it was thou that 5-nitro-1 : 2-dimethylglyoxaline might react with benzaldeh to yield 5-nitro-2-styryl-1-methylglyoxaline under the conditi used by Windaus and Langenbeck (*Ber.*, 1923, **56**, 683) for conve ing 4(5)-nitro-5(4)-methylglyoxaline into 4(5)-nitro-5(4)-styrylg

* It is shown in the experimental part that the behaviour of the pai isomerides 4(and 5)-nitro-1 : 5(and 1 : 4)-dimethylglyoxalines is similar.

oxaline, but neither 4- nor 5-nitro-1 : 2-dimethylglyoxaline reacted with benzaldehyde, and the result calls to mind an unsuccessful attempt to condense 2-methylglyoxaline-4(5)-sulphonic acid with benzaldehyde (Forsyth, Moore, and Pyman, J., 1924, **125**, 919).

5(4)-Bromo-4(5)-nitro-2-methylglyoxaline (IV) is very easily converted into the ammonium salt of 4(5)-*nitro*-5(4)-*thiol*-2-*methylglyoxaline* (V) by means of ammonium sulphide.



Experimental.

The 4- *and* 5-*Nitro*-1 : 2-*dimethylglyoxalines.*

(A) *Preparation by Nitration of* 1 : 2-*Dimethylglyoxaline.*—Concentrated sulphuric acid (6 c.c.) was added to 1 : 2-dimethylglyoxaline (3 g.) in nitric acid (6 c.c.; *d* 1·4) at 0°, the product heated for 4 hours at 100°, cooled, and aqueous sodium hydroxide added, when nearly pure 4-nitro-1 : 2-dimethylglyoxaline (0·5 g.) separated. Chloroform extracted from the filtrate a mixture of bases which was separated by ether into sparingly soluble and readily soluble fractions (0·9 and 2·0 g.), the latter consisting largely of 1 : 2-dimethylglyoxaline. After fractional crystallisation as picrate or base, there were isolated in almost pure condition 4-nitro-1 : 2-dimethylglyoxaline (yield 20% *), 5-nitro-1 : 2-dimethylglyoxaline (yield 10%), and unchanged 1 : 2-dimethylglyoxaline (yield 22%).

(B) *Preparation by Methylation of* 4(5)-*Nitro*-2-*methylglyoxaline.*—4(5)-Nitro-2-methylglyoxaline (20 g.) and methyl sulphate (16 c.c.) were heated for 1 hour at 100°, and the products worked up as in analogous cases described previously (*e.g.*, J., 1922, **121**, 2616), when 2·0 g. of 4(5)-nitro-2-methylglyoxaline were recovered, whilst 5-nitro-1 : 2-dimethylglyoxaline was isolated as picrate (33 g., pure, yield 57%), and 4-nitro-1 : 2-dimethylglyoxaline as base (0·25 g., pure, yield 1·1%).

4-*Nitro*-1 : 2-*dimethylglyoxaline* (III) crystallises from alcohol in glistening needles, m. p. 182—183° (corr.). It is easily soluble in alcohol, somewhat sparingly soluble in cold water, and sparingly soluble in ether (Found: C, 42·4; H, 5·0. $C_5H_7O_2N_3$ requires C, 42·6; H, 5·0%).

The *hydrochloride* is obtained on spontaneous evaporation of a solution of the base in concentrated hydrochloric acid in long needles which on rapid heating sinter at about 175° and melt with

* The compounds described in this paper were colourless, and yields are given in percentage of the theoretical, except where it is stated to the contrary.

effervescence at about 215°. It dissociates on heating at 100° or on treatment with water, giving the base. The base did not yield a picrate.

5-*Nitro*-1 : 2-*dimethylglyoxaline* (II) crystallises from water in long, stout needles, m. p. 138—139° (corr.). It is easily soluble in alcohol, and somewhat sparingly soluble in cold water or ether (Found : C, 42·4; H, 5·1. $C_5H_7O_2N_3$ requires C, 42·6; H, 5·0%). The *hydrochloride* crystallises from dilute hydrochloric acid in large prisms, m. p. 195° (decomp.; corr.) after sintering earlier. It is very easily soluble in water or alcohol, but sparingly soluble in acetone. It is not dissociated by water, and remains unchanged in m. p. after prolonged heating at 100°, but the salt is slowly volatilised. The *picrate* crystallises from water or alcohol in yellow needles, m. p. 162—163° (corr.). It is very sparingly soluble in these solvents when cold (Found : C, 35·8; H, 3·0. $C_5H_7O_2N_3,C_6H_3O_7N_3$ requires C, 35·7; H, 2·7%).

4(5)-*Nitro*-1 : 2 : 3-*trimethylglyoxalinium iodide* is formed on heating methyl iodide with 5-nitro-1 : 2-dimethylglyoxaline at 100° (but not on heating under reflux), or with 4-nitro-1 : 2-dimethylglyoxaline at 150° but not at 100°. It crystallises from alcohol in bright yellow needles, m. p. 195—196° (decomp.; corr.). It is soluble in water and rather less so in cold acetone (Found : I, 44·8. $C_6H_{10}O_2N_3I$ requires I, 44·9%). On heating this salt (3 g.) over a free flame under 33 mm. until distillation began, and crystallising the combined distillate and residue from alcohol, 4-nitro-1 : 2-dimethylglyoxaline (1·0 g., m. p. 179—180°, yield 67%) was obtained.

Attempted Condensations with Benzaldehyde.—Both 4- and 5-nitro-1 : 2-dimethylglyoxalines were recovered to the extent of 90% unchanged after heating 1 g. with benzaldehyde (2 c.c.) and piperidine (0·2 c.c.) for 2 hours at 155—160° under reflux.

Reduction of 5-*Nitro*-1 : 2-*dimethylglyoxaline.*—To a solution of the base (14 g.) in concentrated hydrochloric acid (50 c.c.), a solution of hydrated stannous chloride (68 g.) in concentrated hydrochloric acid (150 c.c.) was added below 10°. After keeping over-night, tin was removed by hydrogen sulphide, when partly crystalline hydrochlorides were obtained. On extraction with absolute alcohol, ammonium chloride (6 g.) remained undissolved; the extract was then added to a solution of picric acid (25 g.) in hot water (1 l.), when picrates were deposited from which after repeated crystallisation from water and alcohol, 1·5 g. of a *picrate*, m. p. 142·5° (corr.), were obtained (Found : C, 39·7, 39·4, 39·1, 39·1; H, 3·7, 4·0, 3·9, 3·8. N, 21·7, 21·7, 21·4. $C_5H_{10}N_2,C_6H_3O_7N_3$ requires C, 40·4; H, 4·0; N, 21·4%). The mother-liquor was extracted with ether to remove

picric acid, and evaporated to dryness, when about 7 g. of partly crystalline hydrochlorides were obtained. These were separated by the method used by Hazeldine, Pyman, and Winchester (*loc. cit.*, p. 1435) into ammonium chloride (1·0 g.), crude methylamine hydrochloride (1·6 g. containing 54·0% Cl) and the hydrochloride of glycine ethyl ester (0·8 g., m. p. 136—140°), yielding the pure substance, m. p. 143—144° (corr.; alone or mixed with a synthetic specimen).

4(5)-*Nitro*-5(4)-*thiol*-2-*methylglyoxaline* (V).—Hydrogen sulphide was passed through a warm solution of 5(4)-bromo-4(5)-nitro-2-methylglyoxaline (2 g.) in 5*N*-ammonia (15 c.c.) for $\frac{1}{4}$ hour, when the *ammonium* salt of 4(5)-nitro-5(4)-thiol-2-methylglyoxaline separated in deep yellow prisms * (1·7 g., yield almost theoretical). It is readily recrystallised from water, and both the crude and the purified material darken from 190°, being quite black by 210° (corr.). This salt is anhydrous, and yields ammonia when boiled with aqueous sodium hydroxide (Found: C, 27·6; H, 5·0; N, 31·9; S, 18·3. $C_4H_8O_2N_4S$ requires C, 27·3; H, 4·5; N, 31·8; S, 18·2%). On rendering its aqueous solution faintly acid with hydrochloric acid, 4(5)-*nitro*-5(4)-*thiol*-2-*methylglyoxaline* is obtained as a yellow, crystalline precipitate, m. p. *ca.* 260° (corr.; decomp.) crude or after crystallisation from alcohol (Found: C, 30·3, 29·8; H, 3·5, 3·2. $C_4H_5O_2N_3S$ requires C, 30·2; H, 3·1%). It is sparingly soluble in alcohol or hot water, and readily soluble in alkalis, ammonia, and sodium carbonate, giving bright yellow solutions, whilst sodium hydroxide gives an orange-yellow solution, which reddens on keeping. It dissolves in 5*N*-hydrochloric acid, but the solution soon deposits pale buff crystals of the hydrochloride, m. p. *ca.* 260° (corr.; decomp.), which dissociate on treatment with water.

4(5)-*Nitro*-1 : 3 : 5(4)-*trimethylglyoxalinium iodide* is formed on heating methyl iodide with 5-nitro-1 : 4-dimethylglyoxaline under reflux or with 4-nitro-1 : 5-dimethylglyoxaline at 100° (but not under reflux). It crystallises from acetone in bright yellow, prismatic needles, m. p. (of material dried at 100°) 134—135° (corr.), and is readily soluble in water or alcohol, but sparingly soluble in cold acetone (Found: loss in a vacuum, 2·9. $C_6H_{10}O_2N_3I,\frac{1}{2}H_2O$ requires H_2O, 3·1. Found, in dried salt: I, 44·9. $C_6H_{10}O_2N_3I$ requires I, 44·9%). After heating the air-dried salt (6 g.) under diminished pressure until all methyl iodide was removed, and crystallising the residue from water, 4-nitro-1 : 5-dimethylglyoxaline (2·42 g., pure, yield 83%) was obtained, whilst the mother-liquors, after being mixed with picric acid and seeded with 5-nitro-1 : 4-dimethylglyoxaline picrate, deposited a minute quantity of a crystal-

* The formation of crystals in this way was first observed by Mr. L. Light, B.Sc.Tech.

line picrate. 4-Nitro-1 : 5-dimethylglyoxaline dissolves in concentrated hydrochloric acid, but after spontaneous evaporation in the air the base remains. On adding water to the solution of the base in concentrated hydrochloric acid, the base is precipitated.

5-*Nitro*-1 : 4-*dimethylglyoxaline hydrochloride* crystallises from dilute hydrochloric acid in prisms, which, after drying at 100°, melt and decompose at 188° (corr.). It slowly volatilises at 100°. After evaporation with water it can be recovered unchanged.

One of us (V. K. B.) desires to thank the University of Bombay for a Sir Mangaldas Nathubai Technical Scholarship which has enabled him to take part in the investigation.

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CCXLIV.—*Some Physical Properties of Aniline and its Aqueous Solutions.*

By MALCOLM PERCIVAL APPLEBEY and PERCIVAL GLYN DAVIES.

IN the course of work on the osmotic properties of aniline solutions (see following paper) the authors have had occasion to prepare this liquid in a pure condition and to make some measurements of its principal properties, as well as to investigate the effect of water upon those properties.

The aniline, purified from thiophen compounds by the method of Hantzsch and Freese (*Ber.*, 1894, **27**, 3), was finally dried over solid potash and fractionated in an apparatus shielded from atmospheric moisture and carbon dioxide by soda-lime tubes. It showed no brown colour, but had a bright blue fluorescence and boiled well within half a degree. The fluorescence disappeared in the course of a few days, even when the liquid was kept in closed brown stoppered bottles in a desiccator in a dark cupboard.

The physical properties of purified aniline have been measured by Timmermans (*Proc. Roy. Soc. Dublin*, 1912, **13**, 326), Knowles (*J. Ind. Eng. Chem.*, 1920, **12**, 881), Schwers (*J. Chim. Phys.*, 1911, **9**, 15), and Tyrer (J., 1911, **99**, 872; 1912, **101**, 84). Their values are compared with ours in the following table :—

	Applebey and Davies.	Timmermans.	Knowles.	Schwers.	Tyrer.
F. p.	−5·98°	−6·2°	−6·24°	—	—
B. p.	184° (appx.)	184·40°	184·32—184·39°	—	—
$d_4^{t°}$	1·02315 (20°)	1·03909 (0°)	1·0268 (15°)	1·02479 (17·6°)	1·02840 (12·87°) 1·02225 (21·89°)
$n_D^{20°}$	1·58685	—	1·5850	—	—

The freezing points recorded by other workers are in each case lower than that observed by us. The differences are in our opinion due in all probability to the care we have taken to exclude water. Aniline, like many other organic liquids, takes up small quantities of water with extreme avidity. Our value for the freezing point is confirmed by the work of Ampola (*Gazzetta*, 1895, **27**, i, 35), who obtained — 5·96°, and our value for the refractive index is somewhat supported by the determinations of Brühl and Weegman (compare Landolt-Börnstein, "Tabellen"), both of whom obtained values of $n_D^{20°}$ considerably higher than that of Knowles. The lower freezing point recorded by Knowles would correspond to about 0·1% of water, the refractive index to about 0·7%, assuming the values now obtained to be the correct ones. The various values recorded in the above table for the relative density, though they differ considerably among themselves, lie upon a fairly smooth curve when plotted against the temperature of determination. This is not surprising, since the relative density, while much affected by changes of temperature, is hardly altered by the addition of water as will be shown later.

Density.—Density measurements were made in pyknometers of about 10 c.c. capacity, weighed against sealed counterpoises in the manner described by Hartley and Barrett (J., 1911, **99**, 1072). The pyknometers were filled by slow suction so as to avoid air bubbles, any filling which showed signs of air bubbles or dust being discarded. The filling with aniline occupied about 15 minutes, so that the possibility of absorption of water vapour from the air during filling had to be considered. By filling at rates varying from 10 to 40 minutes, however, no variation of density of the same sample could be detected. It may therefore be assumed that the water absorbed in this time has a negligible effect on the density. Further, careful determinations with a specific gravity bottle, which can be filled much more quickly, gave results in close agreement with the pyknometer determinations. The value obtained for pure aniline was $d_{20°}^{20°} = 1·02315$ or $d_{4°}^{20°} = 1·02136$.

The density of a saturated solution of water in aniline at 20° was found to be $d_{20°}^{20°} = 1·02393$. (The solution used for this determination was prepared in a thermostat, left to settle for several days, and kept at 25° during filling in order to avoid separation of phases.) Thus about 5% of water produces a density-change of only 0·00078.

Refractive Index.—The refractive indices of pure aniline and of some solutions were determined for sodium light by means of a Pulfrich instrument. The liquids were warmed to about 25° and determinations were made during subsequent cooling. The refrac-

tive indices at 20° were read off the resulting refractive index-temperature curves. These curves were all nearly linear, the temperature coefficient in each case being very near to — 0·00030 per degree.

% Water	0·0	1·0484	2·1232	3·0571
$n_D^{20°}$ obs.	1·58685	1·58396	1·58114	1·57861
$n_D^{20°}$ calc.	—	1·58402	1·58112	1·57860

The refractive index is a linear function of the percentage composition, as is seen from the last column, which is calculated from the equation $n_D^{20°} = 1{\cdot}58685 - 0{\cdot}00270p$, where p is the percentage of water. The change of refractive index with composition is, however, quite small.

Viscosity.—The viscosities of aniline and of some solutions were measured in three viscosimeters. One, which had a time of flow of about 60 minutes with pure aniline, had been standardised by the method previously described by one of us (J., 1910, **97**, 2000) and found to obey Poiseuille's law accurately. The others, which had times of flow of 45 and 15 minutes respectively, gave the same values for the ratio Time of flow for aniline/Time of flow for water as the standard instrument and therefore were in accord with Poiseuille's law. Using freshly distilled aniline for each determination, values for the time ratio were found varying about a mean value of 4·309. Using Thorpe and Rodger's value for the viscosity of water at 20°, this gives the absolute viscosity of aniline as 0·04468, a value almost identical with that obtained by Poiseuille (0·04467) but considerably higher than the later determinations by Faust (0·433 at 18°) (*Z. physikal. Chem.*, 1912, **79**, 99). No great weight can, however, be attached to these determinations, since it was found that the viscosity of pure aniline is not a constant quantity. The variability of the results obtained and the fact, which further investigation brought to light, that freshly distilled aniline suffers appreciable change in viscosity when kept, even when it is stored in a desiccator in the dark, show that some change takes place after distillation. As an example, aniline kept for a week after distillation had a viscosity of 0·04439, nearly 1% less than that of the freshly distilled sample. The change was not due to absorption of water, since the freezing point showed no depression. The aniline was still fluorescent, though it should be noted that the action of light does produce a further slight change of viscosity.

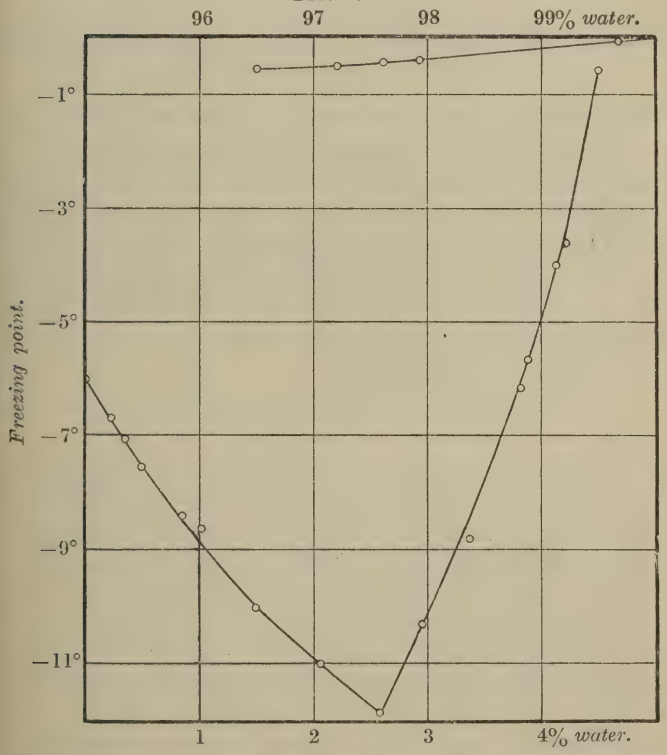
The viscosities of two solutions were measured; they were made up with freshly distilled aniline and gave the following results :—

% Water	0·227	0·344
$\eta^{20°}$	0·0441	0·0438

Freezing Points.—The freezing points were measured in a Beckmann apparatus. The temperatures were in each case determined with different amounts of supercooling, and the accurate freezing points (with no supercooling) estimated from the resulting curve.

% Water.	F. p.	% Water.	F. p.
0	— 5·980°	3·372	—8·80°
0·227	— 6·675	3·820	—6·15
0·344	— 7·050	3·880	—5·65
0·489	— 7·550	4·127	—4·00
0·848	— 8·400	4·219	—3·60
1·015	— 8·625	(congruent	
1·490	—10·000	solutions)	—0·60
2·059	—11·000	97·203	—0·50
2·575 (eutectic)	—11·85	97·608	—0·43
2·952	—10·30	97·928	—0·38

FIG. 1.



The results are plotted in Fig. 1. It will be seen that the eutectic is on the aniline side, the solid separating from solutions containing more than 2·575% of water being ice. The determinations on the ice side of the eutectic were confirmed and extended by Miss E. M. O. Tarrow, to whom our best thanks are due. They are necessarily

somewhat uncertain, since in this region a small separation of soli brings about a relatively large change of concentration.

Taking 58·7 as the cryoscopic constant for aniline (Ampola Rimatori, *Gazzetta*, 1897, **27**A, 35), the calculated molecular weigh of water rises from 22·9 in very dilute solution to 25·1 in a solutio in the neighbourhood of the eutectic. There is thus clear evidenc of association of water in aniline solution. The freezing points c the dilute solutions of aniline in water also indicate association c the solute, the molecular weight calculated being about 105 instea of 93.

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CCXLV.—*Osmotic Pressure by the Solubility Method in Concentrated Solutions.*

By MALCOLM PERCIVAL APPLEBEY and PERCIVAL GLYN DAVIES

THE changes which are produced in the solubility relations of tw partially miscible liquids when a solute is added which is solubl in only one of the liquids have been studied by Nernst and others Nernst has shown that, when the quantities of solute added are s small as to enable the dilute solution relations to be used, th lowering of solubility of the solvent A (which dissolves the solute in the second solvent B is an osmotic property, connected with th osmotic pressure by the relation

$$P = \frac{L - L'}{L'} \cdot \frac{0{\cdot}0819T \,.\, 1000d}{M_0}$$

in which P is the osmotic pressure (through a membrane permeabl to solvent A), L is the solubility of solvent A in solvent B, L' th altered value of L when the solvent A contains the solute, while d and M_0 are the density and molecular weight of solvent A. Th correctness of this expression and its usefulness as a method o molecular-weight determination have been sufficiently proved b Nernst's experiments (*Z. physikal. Chem.*, 1890, **6**, 16) and by thos of Tolloczko (*ibid.*, 1896, **20**, 389) and Küster (*Ber.*, 1894, **27**, 324) These experiments, however, throw no light on the behaviour o strong solutions. The osmotic relations of such solutions can a present only be investigated by means of the direct method or by means of vapour-pressure measurements and the application o Porter's relation (*Proc. Roy Soc.*, 1907, A, **79**, 519). Of these the direct method is not only costly, but also is only applicable fo the very limited range of substances for which a suitable membran

an be found. The vapour-pressure method, on the other hand, is borious and also requires for the solution of the integral terms of orter's equation far more information as to the specific volumes nd compressibilities of solution, solvent, and vapour than is sually available. It therefore seemed worth while to investigate he phenomenon of solubility lowering in strong solutions in the ope of opening up another way of approach to the osmotic relations strong solutions.

The osmotic behaviour of sucrose in aqueous solution has been much more thoroughly studied than that of any other substance hat any experiments on other osmotic properties must begin with his system. The problem of choice of materials accordingly resolves self into finding a second solvent which can be obtained pure, hich dissolves fairly large (and therefore determinable) quantities water and in which sucrose itself is insoluble. The solvent which est fulfils these requirements is aniline, which may be obtained a standard and highly purified condition. It dissolves about % of water at 20° and has no appreciable solvent effect on sucrose. he aniline, which was obtained from Kahlbaum or Merck, was urified in the manner described in the preceding paper. In all ases, however, the aniline was redistilled not more than 3 days efore use. Its purity was frequently tested by determining its eezing point. The freshly distilled aniline froze at $-5{\cdot}98°$; any amples which showed a lower freezing point than $-6{\cdot}1°$ were ried over potash and redistilled.

The water used was twice redistilled from a well-steamed-out ass still and collected in a receiver protected from dust and other mospheric contamination. The sucrose was Kahlbaum's purest roduct, powdered and dried in a sulphuric acid desiccator before use.

The solutions were prepared by stirring weighed quantities of queous solutions of sucrose of known content with measured uantities of aniline in a mercury-sealed stirring bottle of brown ass. The bottle was immersed in a thermostat maintained at $0° \pm 0{\cdot}01°$. The stirring was continued for a day and the solutions ere then left over-night in the thermostat to settle. The aniline hase was removed by means of a dry pipette in experiments where constituted the upper layer, or by a syphon tube when its density as greater than that of the aqueous phase. In the latter case the ifficulty of introducing the syphon without entrapping some of the pper layer was overcome by having the end of the syphon blown ut into a thin closed bulb which could be broken against the ottom of the vessel after the syphon was in position. The solutions ere then centrifuged in a room the temperature of which never iffered by more than a degree from 20°, so as to remove the last

particles of aqueous phase remaining. The method of centrifugin carried out at temperatures differing from the exact experiment temperatures is clearly only permissible when the amount o aqueous phase remaining is negligibly small. It is obvious als that it cannot be used for aniline phases in equilibrium with pur water or very dilute solutions. Other methods have to be use in these cases to obtain complete separation.

Determination of Concentration of Equilibrium Solutions.—It wa hoped that some one of the physical properties of aniline might b sufficiently sensitive to the addition of water to enable the com position of solutions to be estimated by careful measurement o the property. Accordingly the variations of density, refractiv index, viscosity, and freezing point produced by the addition o water were determined. For one cause or another, all thes measurements proved unsuitable. The effect of water on th density and refractive index of aniline is too small; the viscosity i untrustworthy owing to changes occurring with time; and th freezing point is inaccurate as a measure of concentration over th range of the present experiments, since the solid phase separatin consists of the component present in small concentration. Detail of these measurements will be found in the preceding paper.

In these circumstances recourse was had to direct solubilit measurements. Weighed quantities of the solutions, freed fron the aqueous phase by centrifuging, were sealed up in glass tube either alone or with weighed quantities of water added. The tube were shaken in well-stirred water of slowly changing temperature and the temperatures at which turbidity occurred on cooling an disappeared on heating were determined. These temperature differed by not more than 0·2° and the mean was taken to be th temperature of saturation. As there is difficulty in deciding upon a safe criterion of transparency, and as our experience showed tha the results depend to a certain extent upon the conditions of lightin of the tubes, it was thought advisable first to construct a solubilit curve by measuring the temperatures of saturation of known mixture of aniline and water, and to use this curve in interpreting our result rather than the determinations of Sidgwick, Pickford, and Wilsdo (J., 1911, **99**, 1122). The following results were obtained, t being th temperature of saturation :

% Water	4·534	4·659	4·815	4·926	4·950	5·398	5·899	6·104
$t°$	15·9	18·3	20·5	21·15	22·6	34·1	43·5	47·5

A smoothed curve was drawn representing these measurements and used in the subsequent determinations. The saturated solution at 20° from the curve appears to contain 4·835% of water, whereas

idgwick, Pickford, and Wilsdon give 5·123%. The discrepancy ıay be due in part to difference in the aniline used, but is more robably to be ascribed to differences in the conditions of deter- ıining the saturation temperatures. It is of no great moment for ur purpose, as only comparative measurements are in question. .s an example of the consistency of the results obtained in measuring ıe amount of water in the equilibrium solutions, details are given f the analysis of the aniline phase in equilibrium with a solution f 420 g. of sucrose in 1000 g. of solution.

Wt. of solution (g.).	Water added (g.).	Temp. of satn.	% Water in original soln.
—*	0·0	9·5°	4·57
2·1163	0·0241	39·9	4·53
1·6367	0·0098	27·8	4·56
			Mean 4·55

* The solution in this experiment was not weighed and the temperature as determined in an open tube. The agreement with the other experiments ıows that losses during sealing are of no importance.

The method was also tested on two occasions by shaking pure ıiline and water in the thermostat at 20°, allowing to stand in ıe thermostat for a fortnight (the method of centrifuging cannot e used in this case), and determining the temperature of saturation f the aniline layer in unsealed bulbs. The two experiments gave 0·2° and 20·5°, temperatures sufficiently near to 20° to show that ıe method was satisfactory; if complete separation by centrifuging ad been possible, no doubt an even better agreement could have een obtained.

The equilibrium experiments are summarised in the following ıble :

Conc. of sugar soln.		Conc. of water.		Osmotic press. (atm.).		
g./1000 g. of solution.	g./litre.	g./g. of solution.	Mol. fraction.	From Nernst.	Detd.	Calc.
0	0	0·04835	0·2078	—	7·4	5
300	348·1	0·0466	0·2016	50	40	43
420	498·4	0·0455	0·1976	83	69	67
540	676·1	0·0439	0·1917	135	119	103
660	872·8	0·0407	0·1797	250	218	180

'he values for the osmotic pressures in the sixth column are derived ·om the determinations of Berkeley and Hartley (*Phil. Trans.*, 906, **206**, A, 481; 1919, **218**, A, 344), allowance being made for he difference of temperature and for the presence of aniline in he aqueous phase.

It will be noted that the Nernst dilute solution formula soon egins to diverge from the experimental values when the concen- ration becomes fairly large. In the following pages an attempt is

made to relate the solubility lowering to the osmotic pressure solutions outside the range of the dilute solution law.

Since the two solutions, of sugar in water and of water in aniline are in equilibrium, they must have the same osmotic pressure through a membrane permeable to water. Now the aniline phase is an extremely concentrated solution of aniline in water of the osmotic pressure of which we know nothing. There is, however an exact relation between the osmotic pressure of a solution measured by a membrane permeable to one of its constituents and the conjugate osmotic pressure measured by a membrane permeable to the other constituent. This relation, deduced by Berkeley and Burton (*Phil. Mag.*, 1909, **17**, 598), takes the form of a differential equation

$$\frac{dP_1}{dc_2} = \frac{c_2 u_2}{c_1 u_1} \frac{dP_2}{dc_1},$$

in which P_1 = ordinary osmotic pressure–water membrane; P_2 = conjugate osmotic pressure–aniline membrane; c_1 = g. of solvent (water) per g. of solution; c_2 = g. of solute (aniline) per g. of solution; u_1 and u_2 = specific volumes of solvent and solute respectively.

Now the solutions in question, though they are concentrated solutions of aniline in water, are dilute solutions of water in aniline and it might therefore be supposed that they would obey the dilute solution law $P_2 = RTc_1$ and therefore $dP_2/dc_1 = RT$, in which case Berkeley and Burton's expression can be integrated, giving

$$P_1 = -RT\frac{u_2}{u_1}(\log c_1 + c_2),$$

the constant of integration being zero, since $P_1 = 0$ when $c_2 = 0$ and $c_1 = 1$. This method of interpreting the solubility results was suggested to us by the late Dr. C. V. Burton, and gives at once a value for the osmotic pressures of the sugar solutions. Unfortunately, however, the calculations give results which are widely at variance with the known osmotic pressures of these solutions, and the only conclusion which can be drawn is that the assumption that the conjugate osmotic pressures obey the dilute solution law is very far from being true for saturated solutions of water in aniline. The true value of dP_2/dc_1 must in fact be very much less than RT. The same conclusion may be clearly drawn from many experiments on the freezing points of systems consisting of partially miscible liquids. For example, the curves found by Sidgwick and Turner (J., 1922, **121**, 2257) for the temperatures of separation of *o*- and *m*-chlorophenol in presence of increasing quantities of water bend very definitely upward and appear to meet

ıe liquid–liquid line almost horizontally, *i.e.*, with a very small ılue of dT/dc and therefore of dP/dc. The same upward curvature ay be observed in the curve for the separation of solid aniline om aqueous solutions (see preceding paper), but not so clearly this case, since the eutectic intervenes before the curvature has ecome very pronounced.

Although this method of treatment, in the form suggested by urton, has proved inadequate to represent the solubility results, has been found that the application of van Laar's well-known uation for concentrated solutions in place of the dilute solution w gives much more satisfactory results. Assuming that this uation represents the conjugate osmotic pressures, we have $_2 = -RT \log (1 - c_1) + \alpha c_1^2$. Differentiating and substituting the Berkeley–Burton equation,

$$\frac{dP_1}{dc_2} = \frac{c_2 u_2}{c_1 u_1}\left(\frac{RT}{1 - c_1} + 2\alpha c_1\right)$$

hich, since $c_2 = 1 - c_1$, becomes

$$\frac{dP_1}{dc_2} = \frac{u_2}{u_1}\left(\frac{RT}{1 - c_2} + 2\alpha c_2\right),$$

ı expression which on integration gives

$$P_1 = u_2/u_1(-RT \log \overline{1 - c_2} + \alpha c_2^2).$$

he integration constant is again zero.)

This expression is not without interest, since it shows that if the dinary osmotic pressure of a solution can be represented by van aar's expression, so also can the conjugate osmotic pressure, and ith the same value for the constant α, which according to van Laar connected with the mutual attraction of solvent and solute.*

* Mr. D. L. Chapman has pointed out to us that the argument may be ıt more generally thus. If the product of the osmotic pressure of a solution ıd the specific volume of the solvent is a function $f(c)$ of its concentration, en the equation of Berkeley and Burton may be written $(1 - c)\frac{df(c)}{dc} = \frac{f(1 - c)}{d(1 - c)}$, where c is written for c_2 and $1 - c$ for c_1. This is a differential uation which has many solutions, of which, however, the only simple ones e $f(c) = k \cdot \log (1 - c)$ and $f(c) = k'c^2$, k and k' being constants. Putting $= -RT$ in the first solution, we have van Laar's equation $P = -RT \log (1-c)$, duced thermodynamically; taking both solutions together and putting $= \alpha$, we have van Laar's second expression $P = -RT \log (1 - c) + \alpha c^2$, which the second term had a somewhat empirical basis. It is of some portance that this second term is now shown to be a solution of the thermo- namic equation of Berkeley and Burton. We may note also that the lute solution law $P = RTc$ does not satisfy the requirements of this method deduction, and this law accordingly has no validity except as an approxima- on to the true law in conditions of extreme dilution.

The application of the new integration to the foregoing solubili results can only be performed in a somewhat approximate manne since the evaluation of the constant α requires a systematic stud of the osmotic pressures of aniline solutions. A preliminary valu for α can, however, be obtained by assuming the correctness of th osmotic pressure of a saturated solution of water in aniline, whic was calculated (from the lowering of the freezing point) by th usual formulæ as 7·4 atmospheres. The value of R in the expressio is not the usual value, since concentrations are expressed in gram per gram of solution, but may be obtained by assuming that $N/1000$-solution has an osmotic pressure of 0·0224 atm. at 0°; fo such a solution the α term is negligible. With the values thu obtained, *viz.*, $R = 4{\cdot}76$, and $\alpha = 4661$, the values tabulated i the last column of the table were obtained. It will be seen tha the agreement with the direct determinations of Berkeley an Hartley is fairly satisfactory up to a concentration of 420 g. pe 1000 g. of solution, but considerable divergence occurs at high concentrations. Better agreement can be obtained by adjustment o the constants, but since in any case the osmotic pressure is given a the rather small difference of two large terms, such adjustments hav no value except in providing what then becomes a purely empiric equation to express the results.

For the practical determination of osmotic pressures in con centrated solutions the solubility method is not yet capable of givin direct results accurately, though the van Laar integration is a ste towards that end. On the other hand, comparative results ma be obtained without undue experimental difficulty. By findin the percentage of water in the aniline phase in equilibrium with solution of unknown osmotic pressure and reading off from ou results the concentration of the sucrose solution which is in equil brium with the same aniline solution we may at once equate th osmotic pressure of the unknown solution to that of the sucros solution. The method is of course only applicable to solutions o substances the solubility of which in aniline is very slight.

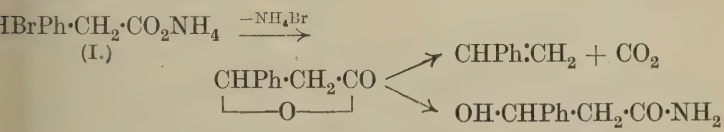
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CXLVI.—*Studies on the Walden Inversion. Part IX. The Influence of the Solvent on the Sign of the Product in the Conversion of β-Bromo-β-phenylpropionic Acids into β-Hydroxy-β-phenylpropionamides.*

By George Senter and Allan Miles Ward.

the reaction between concentrated aqueous ammonia and bromo-β-phenylpropionic acid, no β-amino-β-phenylpropionic acid obtained, but the products consist of β-hydroxy-β-phenylopionamide, styrene, ammonium bromide, and ammonium rbonate (Posner, *Ber.*, 1905, **38**, 2316). The yield of β-hydroxyphenylpropionamide is, however, not good, but is the better the gher the concentration of ammonia employed. These results ould lead to the view that this reaction proceeds *via* the correonding lactone, thus :



In the present experiments the reaction of ammonia in ethyl cohol, in acetonitrile, and also of liquid ammonia with *r*-β-bromophenylpropionic acid have been investigated, and in each case e hydroxyamide (III) was produced, together with styrene, but no amino-β-phenylpropionic acid was isolated. These reactions in n-aqueous solvents are in accordance with the mechanism given ove. The reaction of β-bromo-β-phenylpropionic acid with mmonia in dry ethereal solution yields a precipitate of (I), and is appears to be the first salt of this acid to be isolated. It is ry unstable, dissolving in water to a clear solution, shortly llowed by a pronounced turbidity due to the production of styrene, d decomposing fairly rapidly in the dry state at room temperature, t the lactone (II) could not be isolated from the products of dry composition. The *diethylammonium* salt underwent similar composition, but with greater ease.

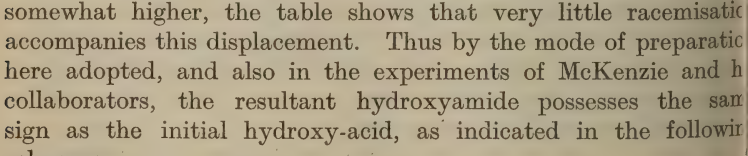
In spite of the failure to isolate the lactone, the mechanism suming its intermediate formation still seems probable from the actions of β-bromo-β-phenylpropionic acid, and also from the haviour of related substances. The view that β-phenyl-β-opionolactone has a transitory existence was first put forward by lenmeyer (*Ber.*, 1880, **13**, 305) to account for the observation of

Fittig (*Annalen*, 1879, **195**, 131) that β-bromo-β-phenylpropio acid reacting with aqueous sodium carbonate yields styrene almo quantitatively. The lactones of all three β-bromo-β-mononitr phenylpropionic acids have been prepared as stable crystalline soli (Einhorn, *Ber.*, 1883, **16**, 2208; Basler, *ibid.*, p. 3001; Prausnit *ibid.*, 1884, **17**, 595). The products of decomposition of these lacton by heat, and also by reaction with ammonia, are of the same typ as those obtained from β-bromo-β-phenylpropionic acid, the on differences being in the relative proportions of the products.

Not only did liquid ammonia, ethyl-alcoholic ammonia, acet nitrile ammonia and aqueous ammonia solutions yield the hydrox amide in each case from the *r*-bromo-acid, but with an optical active bromo-acid as initial material, the hydroxyamide produc by reaction in the above solvents was opposite in sign to the brom acid used, as shown in the following table:

Solvent.	[α] of bromo-acid.	α of amide.	[α] of amic
Liquid ammonia	+74·6°	−1·88°	−27·5°
Ethyl alcohol	−75·1	+1·35	+24·3
Acetonitrile	+81·7	−1·93	−28·2
Water	−85·0	+1·68	+27·8

d-β-Hydroxy-β-phenylpropionamide with [α] + 38·4° in ethy alcoholic solution has been prepared by McKenzie, Rule, ar Martin (J., 1914, **105**, 1588) by the esterification of *d*-β-hydrox β-phenylpropionic acid, followed by reaction with ammoni whilst the *l*-isomeride with [α] − 39·5° was similarly prepared b McKenzie and Smith (J., 1922, **121**, 1359). β-Bromo-β-pheny propionic acid has not been prepared in a state of optical purit McKenzie and Humphries (J., 1910, **97**, 121) obtained an ac with $[\alpha]_D$ + 96·2° by recrystallisation of a bromo-acid with [α + 32·2° from chloroform, whilst in the present experiments an ac with $[\alpha]^{13°}$ + 110° for $c = 1·079$, $l = 2$, was obtained as a final cr by fractional precipitation of the bromo-acid from chlorofor solution by means of ligroin (b. p. 40—60°). This acid being take as optically pure, although possibly the activity of the pure acid somewhat higher, the table shows that very little racemisatio accompanies this displacement. Thus by the mode of preparatio here adopted, and also in the experiments of McKenzie and h collaborators, the resultant hydroxyamide possesses the sam sign as the initial hydroxy-acid, as indicated in the followi scheme:



Walden inversion is not here detected by solvent variation, and e only examples yet obtained of either isomeride being produced preponderating amount by solvent variation alone is in the single stance in which phenyl and carboxyl are both attached to the ymmetric carbon atom.

Experimental.

β-Bromo-β-phenylpropionic Acids.—The inactive acid was prepared by Senter and Ward (J., 1924, **125**, 2137), and the active bromo-ids by the conversion of *d*- and *l*-β-hydroxy-β-phenylpropionic ids with hydrogen bromide in glacial acetic acid at 25°, followed y one recrystallisation of the product from chloroform.

Ammonium β-Bromo-β-phenylpropionate.—To 25 c.c. of dry ether reviously saturated with ammonia, 2 g. of finely powdered β-bromo-phenylpropionic acid were added, and shaken for a few minutes. he solid was washed with dry ether and rapidly dried over con-ntrated sulphuric acid. The bromine was estimated by heating weighed sample with aqueous sodium carbonate until styrene as expelled, followed by precipitation as silver bromide (Found : r, 32·1. $C_9H_{12}O_2NBr$ requires Br, 32·5%). This salt undergoes irly rapid decomposition in the dry state at room temperature, and pid decomposition without melting at 60°, the products being mmonium bromide, carbon dioxide, styrene, and a small amount cinnamic acid.

Diethylammonium β-bromo-β-phenylpropionate was prepared by lding diethylamine (1 mol.) to the bromo-acid (1 mol.) in ethereal lution (2—3%), when white, compact crystals soon commenced to parate. The salt was isolated after 15 minutes as in the case of e ammonium salt, and the bromine estimated in the same way ound : Br, 26·6. $C_{13}H_{20}O_2NBr$ requires Br, 26·5%). This salt osely resembles the ammonium salt in properties, but is even more nstable, the temperature of rapid decomposition in the dry state ing 44—45°.

Conversion of β-Bromo-β-phenylpropionic Acids into β-Hydroxy-phenylpropionamides.—The reactions were first carried out with e *r*-bromo-acid, and as in each case β-hydroxy-β-phenylpropion-mide resulted (m. p. 121—122°), together with styrene and mmonium bromide as main products, these experiments are not scribed. The method of experiment with the active acids was follows : The solvent was added to the bromo-acid (5 g.), and ter a definite period the solvent was evaporated on the water-bath (except in 1). The residual solid was extracted with dry ether in Soxhlet apparatus for 10 hours, and the ether evaporated; the oduct consisted of crude β-hydroxy-β-phenylpropionamide. The

insoluble residue in the extractor was analysed for bromine in eac case; the results are shown under (*a*), the theoretical value f ammonium bromide being Br, 81·6%. Under (*b*) are given th yield of crude hydroxyamide, the observed rotation, the specif rotation, and the percentage of nitrogen (determined by dire distillation into standard acid of the ammonia evolved on decon position of the amide by heating with excess of aqueous caustic soda In each case the percentage of nitrogen was appreciably lower tha the theoretical (8·5), and the hydroxyamide was markedly acid i reaction. This acidity was removed by shaking a solution of th crude amide in some 125 c.c. of ether with dilute aqueous caust soda until the aqueous layer was alkaline. The ethereal layer wa separated, the alkaline aqueous solution extracted four times wit ether, the ethereal solutions were combined, and the solvent wa evaporated, when the purified amide remained. Its rotation an analysis are given under (*c*). The remaining aqueous solution in a cases yielded on acidification a small precipitate of cinnamic aci All measurements of rotation were made in ethyl-alcoholic solutio in a 2-dcm. tube with the yellow mercury line.

(1) *Liquid ammonia.* Liquid ammonia (50 c.c.) was added to th *d*-bromo-acid with $[\alpha]^{18^\circ} + 74{\cdot}6^\circ$, when a clear solution quick resulted. This was left in the solid carbon dioxide–ether freezin mixture for ½ hour, when considerable solid had separated. Th solvent was then allowed to evaporate.

(*a*) Br, 81·4%.
(*b*) 0·8 g.; $\alpha^{16^\circ} - 1{\cdot}69^\circ$, $c = 3{\cdot}528$; $[\alpha]^{16^\circ} - 24{\cdot}0^\circ$; N, 8·1%.
(*c*) $\alpha^{22{\cdot}5^\circ} - 1{\cdot}88^\circ$, $c = 3{\cdot}422$; $[\alpha]^{22{\cdot}5^\circ} - 27{\cdot}5^\circ$; N, 8·3%.

(2) *Ethyl alcohol.* Ethyl alcohol (75 c.c.) at − 15°, dried b distillation over lime and saturated with ammonia at − 14°, wa added to the *l*-bromo-acid with $[\alpha]^{15^\circ} - 75{\cdot}1^\circ$. The acid rapid dissolved to a clear solution, and the temperature was allowed t rise slowly. At the end of an hour a considerable precipitate o ammonium carbamate had separated. The solvent was evaporate after 3 hours.

(*a*) Br, 77·5%.
(*b*) 1·6 g.; $\alpha^{15^\circ} + 1{\cdot}60^\circ$, $c = 3{\cdot}644$; $[\alpha]^{15^\circ} + 22{\cdot}0^\circ$; N, 7·3%.
(*c*) $\alpha^{20^\circ} + 1{\cdot}35^\circ$, $c = 2{\cdot}776$; $[\alpha]^{20^\circ} + 24{\cdot}3^\circ$; N, 8·2%.

(3) *Acetonitrile.* Acetonitrile (75 c.c.) at − 18°, saturated wit ammonia at − 13°, was added to the *d*-bromo-acid with $[\alpha]^{1}$ $+ 81{\cdot}7^\circ$. The acid dissolved to a clear solution, from which a heav precipitate of ammonium bromide rapidly separated. The tem perature was allowed to rise slowly, and the solvent was evaporate after 3 hours.

) Br, 71·1%.
) 1·4 g.; $\alpha^{16°} - 2·07°$, $c = 3·868$; $[\alpha]^{16°} - 26·8°$; N, 7·8%.
) $\alpha^{24°} - 1·93°$, $c = 3·422$; $[\alpha]^{24°} - 28·2°$; N, 8·6%.

(4) *Water*. Aqueous ammonia (35 c.c.) saturated at − 10° was ded to the *l*-bromo-acid with $[\alpha]^{12°} - 85·0°$, and kept at − 10° r ½ hour. The acid dissolved to a turbid solution and a con-lerable layer of styrene separated. The solvent was evaporated ter 3 hours.

) Br, 75·9%.
) 1·3 g.; $\alpha^{15°} + 1·55°$, $c = 3·322$; $[\alpha]^{15°} + 23·3°$; N, 7·4%.
) $\alpha^{24°} + 1·68°$, $c = 3·028$; $[\alpha]^{24°} + 27·8°$; N, 8·3%.

One of us (A. M. W.) desires to express his indebtedness to the epartment of Scientific and Industrial Research for a maintenance ant during the course of this investigation.

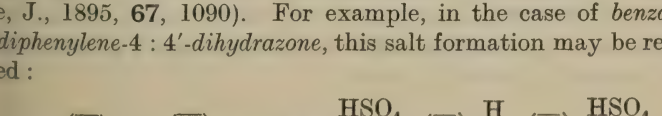
Birkbeck College,
University of London, E.C. 4. [*Received, June 5th*, 1925.]

CXLVII.—*The Colours Produced by the Action of Sulphuric Acid upon Some Hydrazones.*

y Frederick Daniel Chattaway, Stanley John Ireland, and Arthur John Walker.

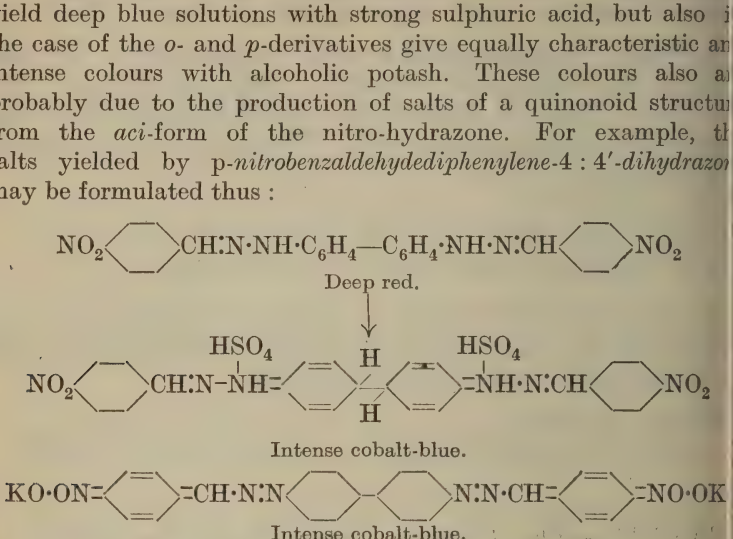
ost hydrazones when dissolved in strong sulphuric acid give loured solutions (Bülow, *Annalen*, 1886, **236**, 194; Pechmann, *er.*, 1893, **26**, 1045; Troeger and Puttkammer, *J. pr. Chem.*, 1908, **3**, 450). These colours are not as a rule very characteristic, or nspicuous, but those given by many of the hydrazones of di-ienylene-4 : 4′-dihydrazine, of *p*-iodophenylhydrazine, and of iodo-2-methylphenylhydrazine are of a peculiarly intense shade cobalt-blue.

These colours are probably due to the formation of salts of a inonoid structure similar to that suggested by Wieland (*Ber.*, 1907, **0**, 4260) to account for the brilliant blue colour produced when tra-*p*-tolylhydrazine is dissolved in sulphuric acid (Chattaway and gle, J., 1895, **67**, 1090). For example, in the case of *benzalde-dediphenylene*-4 : 4′-*dihydrazone*, this salt formation may be repre-nted :



Pale yellow. Intense cobalt-blue.

The *hydrazones* which with *o*, *m*, and *p*-nitrobenzaldehyde for these hydrazines are of special interest, for not only do the yield deep blue solutions with strong sulphuric acid, but also i the case of the *o*- and *p*-derivatives give equally characteristic an intense colours with alcoholic potash. These colours also a probably due to the production of salts of a quinonoid structu from the *aci*-form of the nitro-hydrazone. For example, t salts yielded by p-*nitrobenzaldehydediphenylene*-4 : 4′-*dihydrazo* may be formulated thus :



The nitro-group not being concerned in the production of t salt by sulphuric acid, its position scarcely affects the intensity the character of the colour, all the three isomeric nitrobenzaldehyd hydrazones of diphenylene-4 : 4′-dihydrazine, of *p*-iodopheny hydrazine, and of 4-iodo-2-methylphenylhydrazine giving the san intense cobalt-blue.

In the production of colour by alcoholic potash, however, t nitro-group is involved, and, as with other nitrobenzaldehyd hydrazones, its character depends on the position occupied by th group. Intense colour is produced only by the *o*- and *p*-isomeride these alone yielding salts of the necessary quinonoid configuratio The colour produced follows the rule established for *o*-, *m*-, an *p*-nitrobenzaldehydehydrazones in general (Chattaway and Clem J., 1923, **123**, 3041), that is, the *o*-nitro-hydrazone gives a brig green, the meta- a brown, and the para- an intense blue colour.

It is worth noting that the colours produced by the *p*-nitr benzaldehydehydrazones of these hydrazines with sulphuric ac are practically indistinguishable from the intense blue colours whic they yield with alcoholic potash.

Experimental.

The diphenylene-4 : 4′-dihydrazones (formulæ as I) were prepare by adding a hot acetic acid solution of the appropriate aldehyc

r ketone (2 mols.) to a hot acetic acid solution of diphenylene-
: 4′-dihydrazine (1 mol.). On cooling, the hydrazone separated
s a rule as a microcrystalline powder. Nearly all are so
)aringly soluble in ordinary organic solvents that they cannot
e recrystallised from them. In boiling nitrobenzene, however,
ıey are moderately easily soluble, and separate on cooling in well-
eveloped crystals.

When these hydrazones are added to a large excess of strong
ılphuric acid, intensely coloured solutions are produced. In
)me cases the salts to which the colour is due are comparatively
:able and the colours persist at the ordinary temperature for
)urs or even days with but little change; in others, however,
ecomposition soon occurs and the colour alters in character or
isappears.

After a description of the crystals, the melting point, and the
ıalytical data of the individual hydrazone, the colour produced
ith strong sulphuric acid is given and then the colour produced by
:rong alcoholic potash.

Benzaldehydediphenylene-4 : 4′-*dihydrazone* (I).—Pale yellow
:edles, m. p. 283° (decomp.) (Found : N, 14·6. $C_{26}H_{22}N_4$ requires
, 14·4%). Brilliant cobalt-blue, which slowly fades, leaving after
)me hours only a yellowish-brown liquid. It gives no colour with
coholic potash.

Salicylaldehydediphenylene-4 : 4′-*dihydrazone*.—Pale yellow plates,
. p. 264° (decomp.). Indigo blue, which on warming, or on long
anding becomes green and finally yellow. With alcoholic potash
: gives a brownish-yellow solution.

Anisaldehydediphenylene-4 : 4′-*dihydrazone*.—Pale yellow needles,
. p. 248° (decomp.) (Found : N, 12·4. $C_{28}H_{26}O_2N_4$ requires
., 12·4%). Bright green. With alcoholic potash it gives no
olour.

Cinnamaldehydediphenylene - 4 : 4′ - *dihydrazone*. — Long, yellow
:edles, m. p. 253° (decomp.) (Found : N, 12·6. $C_{30}H_{26}N_4$ requires
., 12·7%). Deep sap-green. With alcoholic potash it yields no
olour.

Acetophenonediphenylene-4 : 4′-*dihydrazone*.—Pale yellow, irregular
jates, m. p. 250° (decomp.). Heliotrope.

Benzophenonediphenylene-4 : 4′-*dihydrazone*.—Yellow plates, m. p.
)5° (decomp.). Brilliant violet, which soon changes on standing
t a dirty, blackish tint.

Pyruvic Acid Diphenylene-4 : 4′-*dihydrazone*.—Yellow, micro-
crystalline powder, m. p. 225° (decomp.). Dark orange-red, which
i a few seconds changes to an intense magenta colour, which
(rkens on standing. Pale yellow solution in alcoholic potash.

o-*Nitrobenzaldehydediphenylene*-4 : 4′-*dihydrazone*.—Dark re needles, appearing almost black by reflected light, m. p. 24 (decomp.) (Found : N, 17·6. $C_{26}H_{20}O_4N_6$ requires N, 17·5% Intense brilliant cobalt-blue indistinguishable in shade from th given by the benzaldehydediphenylenedihydrazone. This colo changes more rapidly than those given by the *m*- and *p*-isomeride and after 15–20 minutes becomes of a greenish or peacock-bl shade, the green shade becoming more marked as time passe until after 1–2 hours the liquid is olive-green, which finally becom yellowish-brown. Deep green solution in warm strong alcohol potash.

m-*Nitrobenzaldehydediphenylene*-4 : 4′-*dihydrazone*.—Compac dark red, octahedral crystals, m. p. 257° (decomp.) (Found : 17·4%). Intense brilliant cobalt-blue solution indistinguishab from that given by its isomerides. The colour changes less readi that than given by its *o*-isomeride, the peacock-blue shade beir developed after about 30 minutes, and changing very little f several hours. Brown solution in alcoholic potash.

p-*Nitrobenzaldehydediphenylene*-4 : 4′-*dihydrazone*.—Deep re slender plates, m. p. 275° (decomp.) (Found : N, 17·65%). Inten blue solution, indistinguishable in shade from that given by its and *m*-isomerides, and by benzaldehydediphenylene-4 : 4′-d hydrazone. It dissolves in alcoholic potash giving a brillia cobalt-blue solution, practically indistinguishable from that give by it and its isomerides with strong sulphuric acid.

Behaviour of the p-*Iodophenylhydrazones with Sulphuric Acid*.—Benzaldehyde-*p*-iodophenylhydrazone dissolves in strong sulphur acid, giving a deep peacock-blue solution. *o*-, *m*-, and *p*-Nitr benzaldehyde-*p*-iodophenylhydrazones when added to stron sulphuric acid give at the moment of contact a yellow or oran colour, which very quickly changes to green, and then again rapid to an intense cobalt-blue, indistinguishable from the colour give by the corresponding diphenylenedihydrazones.

With strong alcoholic potash the benzaldehydehydrazone giv a yellow solution, the *o*-nitrobenzaldehydehydrazone a dee brilliant green, the *m*-nitrobenzaldehydehydrazone a deep cle brown, and the *p*-nitrobenzaldehydehydrazone a brilliant cobal blue, indistinguishable from that given with sulphuric acid.

The o-, m-, and p-*nitrobenzaldehyde*-4-*iodo*-2-*methylpheny hydrazones* behave similarly with strong sulphuric acid. A yello colour momentarily develops, which quickly changes to an inten cobalt-blue. The blue colours are indistinguishable from on another, and from those developed by the corresponding diphenylen dihydrazones.

With strong alcoholic potash similarly the *o*-nitrobenzaldehydehydrazone gives a brilliant green colour, the meta- a clear brown, and the para- a brilliant cobalt-blue, indistinguishable from that given with sulphuric acid.

It is worthy of note that the corresponding hydrazones derived from o- and m-*iodophenylhydrazines* give no intense colours with strong sulphuric acid, only yellow or orange-coloured solutions being obtained. With alcoholic potash, the *o*-nitrobenzaldehydehydrazone gives a deep green, and the *p*-nitrobenzaldehydehydrazone a brilliant cobalt-blue solution.

The Queen's College, Oxford. [*Received, July 9th*, 1924.]

CCXLVIII.—*Studies in the Camphane Series. Part XL. Constitution of Manasse's Hydroxycamphor.*

By Martin Onslow Forster and Prajaram Prabhashanker Shukla.

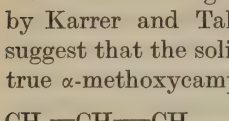
Following his initial description of hydroxycamphor (*Ber.*, 1897, **30**, 659), Manasse further characterised the material formed on reducing camphorquinone (*Ber.*, 1902, **35**, 3811) and claimed to recognise two isomeric substances, indistinguishable in appearance and optical activity; the "α"-modification melted at 203—205° with $[\alpha]_D$ 12·8°, whilst the "β"-modification, produced by hydrolysing the solid methyl ether, melted at 212—213° with $[\alpha]_D$ 12·3°.

It is unfortunate that Manasse denominated his materials in this perplexing manner, because it was already known that replacement of hydrogen in the camphor molecule might occur elsewhere than at the α-position; αβ-dibromocamphor, originally called β-dibromocamphor, was first prepared in 1866 by Swarts and reinvestigated many times after 1881, whilst β-bromocamphor was isolated in 1901. Hence, at the time of publishing his experiments, Manasse might well have been aware that a substance called β-hydroxycamphor would correspond in orientation with β-bromocamphor; confusion with the true β-hydroxycamphor subsequently described (Forster and Howard, J., 1913, **103**, 63) might thus have been avoided.

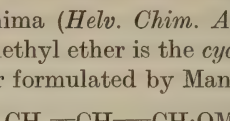
Manasse supported his belief in the existence of two distinct modifications by the production of two oximes, m. p. 86—87° (α) and 83—84° (β), two phenylhydrazones, m. p. 137·5° (α) and 111—113° (β), two semicarbazones, m. p. 182—183° (α) and 202—204° (β) and two benzenesulphonyl derivatives, m. p. 95—96° (α) and 111—113° (β). Excepting the last-named, however, these pairs might have arisen from a single hydroxycamphor, and in view of the

slender distinction between the two parents, one of us (M. O. F.) with Dr. A. Zimmerli began in 1911 an inquiry which was interrupted and could not be resumed until eighteen months ago.

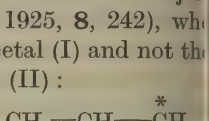
Simultaneous light and shadow have now been cast on the subject by Karrer and Takashima (*Helv. Chim. Acta*, 1925, **8**, 242), who suggest that the solid methyl ether is the *cyclo*acetal (I) and not the true α-methoxycamphor formulated by Manasse (II) :



(I.)



(II.)

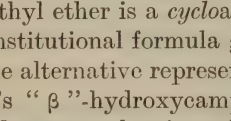


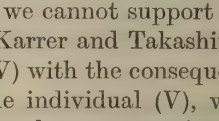
(III.)

Thereupon they propose for Manasse's α-and β-hydroxycamphor the representation (III), ascribing to configuration-change in one of the asterisked carbon atoms the respective divergence in properties.

Our experiments amply confirm the above suggestion that the solid methyl ether is a *cyclo*acetal, but we cannot support the complete constitutional formula given by Karrer and Takashima. We prefer the alternative representation (IV) with the consequence that Manasse's " β "-hydroxycamphor is the individual (V), whilst his " α "-hydroxycamphor is probably that substance associated with a variable amount of the stereoisomeride in which the hydroxyl group and hydrogen atom both occupy the alternate plane.

(IV.)

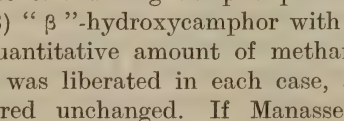




(V.)

With Karrer and Takashima, we agree that the solid methyl ether does not reveal a carbonyl group; we failed to produce an oxime and recovered the substance unchanged by treatment with magnesium methyl iodide. Moreover, on treating separately (1) the crude product of reducing camphorquinone, (2) " α "-hydroxycamphor and (3) " β "-hydroxycamphor with excess of the Grignard agent the quantitative amount of methane required by one hydroxy group was liberated in each case, and the original product was recovered unchanged. If Manasse's hydroxycamphor had the conventional constitution (VI), it could scarcely escape at least partial conversion into the secondary-tertiary diol (VII), in view

(VI.)

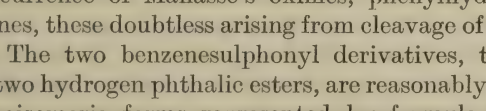


(VII.)

of the readiness with which camphorquinone is transformed into the dimethyldiol by magnesium methyl iodide (Forster, J., 1905, **87**, 241).

Our reason for questioning the transference of the hydroxyl group rom the true α-position (in V) to the adjacent carbon atom (in III), s represented by Karrer and Takashima, is the one familiar to all hemists who have closely studied the members of this family, amely, the greatly superior activity of the α-carbon atom to that of ts ketonic neighbour. The comparative behaviour of camphor and f camphorquinone towards aniline, phenylhydrazine, hydroxyl- mine, semicarbazide, nitromethane, ethyl cyanoacetate, and phenyl- cetonitrile may be recalled in this connexion: and finding that Ianasse's hydroxycamphor is readily formed by reducing a cold thereal solution of camphorquinone with aluminium amalgam, we annot believe that in this reaction alone the diketone has belied tself.

Aside from the question of orientation, however, the above iagnosis by Karrer and Takashima has, in our judgment, clarified situation which has been hitherto most obscure, and harmonises /ith the occurrence of Manasse's oximes, phenylhydrazones and emicarbazones, these doubtless arising from cleavage of the ethylene xide-ring. The two benzenesulphonyl derivatives, to which we ave added two hydrogen phthalic esters, are reasonably attributable o the stereoisomeric forms represented by formula V, because, lthough tertiary alcohols do not generally incur the formation of ydrogen phthalic esters, even limited occurrence of the equilibrium,



/ould account for the result observed. Moreover, the irregular ourse of ester-hydrolysis revealed by the polarimeter indicates the peration of concurrent mutarotation in the hydroxycamphor egenerated.

Experimental.

Reduction of Camphorquinone.—(a) Zinc and acetic acid. Cam- horquinone (40 g.) dissolved in hot glacial acetic acid (70 c.c.) /as precipitated by hot water (500 c.c.), and zinc dust (40 g.) added ı small quantities to the continuously shaken suspension. The lear, pale green liquid was heated to coagulate undissolved zinc, ıe filtrate from which was saturated with salt and allowed to cool. [ydroxycamphor was removed by filtration; after treating the ltrate with just sufficient sodium hydroxide (20%) to redissolve ıe zinc hydroxide, more was extracted by ether (three times), in hich the separated portion was then dissolved. Dried with ılcium chloride, the ether was distilled and left a very pale ellow, camphoraceous residue (32·5 g.; yield 80%).

(*b*) *Aluminium amalgam.* Camphorquinone dissolved in undried ether was left in contact with freshly amalgamated aluminium during 12 hours. The colour faded to very pale green, and the decanted liquid with ether-washings having been dried and distilled deposited a colourless residue (yield 85%).

After crystallisation from petroleum the material prepared by each of the above methods melts at 203—205°; the less readily fusible product described by Manasse has been obtained only by hydrolysing the solid methyl ether. This compound crystallises in colourless plates from a solution of the initial product in methyl alcohol containing hydrogen chloride (6%); it melts at 149—150° (Found: MeO, 15·9. Calc., MeO, 17·0%) and has $[\alpha]_D$ 182·8° (1% in chloroform). The methyl ether is not affected by boiling alcoholic potassium hydroxide (10%), but is rapidly hydrolysed by cold hydrochloric acid, from which sodium carbonate precipitates the less readily fusible form of hydroxycamphor; this melts at 215°, and in all other respects is indistinguishable from the material arising directly on reduction of camphorquinone.

The Hydroxyl Value of Hydroxycamphor. —At one time it seemed possible that the peculiar behaviour of hydroxycamphor might be due to its representing the equilibrium mixture,



but this is now precluded by several indications. In the first place, hydroxycamphor in chloroform does not decolorise bromine, and in ether does not develop a coloration with ferric chloride; moreover, the aqueous solution does not give a precipitate with copper acetate, and the methyl ether is equally indifferent to all these agents. When the action of bromine is pressed by heating hydroxycamphor with the halogen in acetic acid which has dissolved sodium acetate, a very slow action occurs; but this leads to camphoric anhydride without any indication of addition or substitution. The same treatment converts the solid methyl ether also into camphoric anhydride, and in both cases a considerable proportion of unchanged hydroxycamphor is recovered, having survived this attack during several hours.

Conclusive evidence against the above possibility, however, was given by the behaviour of hydroxycamphor towards magnesium methyl iodide, from which the quantitative amount of methane for one hydroxyl group was liberated equally by the crude product of reducing camphorquinone and by specimens of hydroxycamphor melting at 203—205° and at 215°, whilst the methyl ether also

remains unaltered by the Grignard agent without liberating methane. These experiments were conducted in phenetole, and appeared remarkable in view of the observations by Bredt-Savelsberg and others (*J. pr. Chem.*, 1924, **107**, 65) relating to enolisation of camphor by the Grignard agent, which may exceed 40%; but they now receive their explanation in the *cyclo*acetal representation of Karrer and Takashima.

The Camphoryl Hydrogen Phthalates.—A mixture of phthalic anhydride and hydroxycamphor (m. p. 215°) in equal weights, and therefore containing a slight molar excess of the anhydride, was heated at 110—120° during 8 hours and kneaded in a solution of sodium carbonate. On extracting the filtered liquid with ether, about 15% of the hydroxycamphor was recovered unchanged, whilst the hydrogen phthalate was precipitated along with phthalic acid by neutralising the solution of sodium salts; it was separated by dissolution in chloroform, which deposited crystals on evaporation. Recrystallisation from benzene–petroleum gave *camphoryl hydrogen phthalate* in rectangular plates, m. p. 164—165° (Found: C, 68·2; H, 6·6. $C_{18}H_{20}O_5$ requires C, 68·3; H, 6·3%). The $[\alpha]_D$ in aqueous alcohol (1 : 1) was 53·7°.

On repeating this operation with hydroxycamphor melting at 203—205°, or with a specimen recovered unchanged by the methylation process, the proportion of unconverted hydroxycamphor was about the same, and the first crop of crystals melted at 152—156°; this was ultimately resolved into a mixture of the foregoing substance with an isomeric *camphoryl hydrogen phthalate* crystallising in slender needles, m. p. 147° (Found: C, 68·1; H, 6·4%). The $[\alpha]_D$ in aqueous alcohol (1 : 1) was 42·2°.

Thus there appear to be two definite hydrogen phthalates, but it has not been possible to decide whether hydrolysis leads to the respective parents. In fact, on following the hydrolysis polarimetrically, there is an indication of the result being an equilibrium system.

A clear solution prepared by mixing equal volumes of alcohol (97·5%) and aqueous potassium hydroxide (20%) was used. When dissolved in this, the higher-melting hydrogen phthalate passed from the initial $[M]_D$ 102·7° to 61·6° during 200 hours, whilst the isomeride changed from $[M]_D$ 55·0° to 64·4°. Intermediate stages were various, however, the higher-melting form having sunk to $[M]_D$ 60·3° when the isomeride was at 98·6° (after 50 hours), and rising again to $[M]_D$ 73·0° when the isomeride had fallen to 78·3° (after 145 hours). These changes are probably due to varying rates of hydrolysis overlapping unequal mutarotation of the resulting hydroxycamphor, because, in the same alcoholic alkali, higher-melting hydroxycamphor

with initial $[M]_D$ 34·2° reaches a maximum of 82·6° in 26 hours and begins to fall after 48 hours, whilst the lower-melting form has initial $[M]_D$ 50·9°, reaches its maximum of 69·0° at about the same time as the other, and then remains constant. The later observations are only approximate because the liquids, although initially colourless, develop a brown tint which increases in depth with passage of time: moreover, the hydroxycamphor recovered from such solutions melts lower and more indefinitely than the original materials.

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BANGALORE, S. INDIA. [*Received, June 29th*, 1925.]

CCXLIX.—*A New Synthesis of Arylazoaldoximes.*

By THOMAS KENNEDY WALKER.

THE interaction of aryldiazonium salts and malonic acid does not always produce formazyl compounds; thus Busch and Wolbring (*J. pr. chem.*, 1905, **71**, 366) obtained phenylhydrazones of glyoxylic acid from certain ortho-substituted diazonium salts and *o*-chlorobenzeneazoformaldoxime from diazotised *o*-chloroaniline, and the present author found (J., 1923, **123**, 2775) that the interaction of diazotised *p*-nitroaniline and allylmalonic acid produced a mixture of a formazyl derivative with an acidic substance the instability of which precluded its examination. As it seemed probable that this anomalous behaviour might be due to the presence of adventitious nitrous acid, a study was made of the simultaneous action of an aryldiazonium salt and nitrous acid on monoalkylated malonic acids. This resulted in a new synthesis of arylazoalkylformaldoximes, *e.g.*, *benzeneazobenzylformaldoxime* and *benzeneazoallylformaldoxime*. The course of the reaction is probably as follows,

$$CHR(CO_2H)_2 + N_2Ph\cdot OH \xrightarrow[-H_2O]{-CO_2} CO_2H\cdot CR{:}N\cdot NHPh \xrightarrow{+HNO_2} OH\cdot N{:}CR\cdot N{:}NPh + CO_2 + H_2O,$$

since an almost quantitative yield of benzeneazobenzylformaldoxime was obtained by the action of nitrous acid on the phenylhydrazone of phenylpyruvic acid, whereas no condensation occurred when diazobenzene was brought into contact with its oxime.

EXPERIMENTAL.

Benzeneazobenzylformaldoxime.—(*a*) To a diazo-solution (aniline 1·86 g., glacial acetic acid 6 g., concentrated hydrochloric acid 6 c.c.; sodium nitrite 1·38 g., ice-water 35 c.c.) were added benzyl-

malonic acid (3·8 g. dissolved in a little ice-water), crystalline sodium acetate (10·8 g.), and, 5 minutes later (this condition is essential for successful preparation), a cooled 2% aqueous solution of nitrous acid (1·5 mols.) The mixture was filtered and kept cold for 30 hours, during which carbon dioxide was evolved. A solution of the bulky, spongy, yellow product in dilute aqueous caustic potash was filtered from a small quantity of benzylformazyl. The *oxime*, precipitated by 5% acetic acid, was crystallised from 80% acetic acid (in small, deep yellow needles) and then from benzene (in paler, silky needles) by the addition of light petroleum; m. p. 144° (yield, nearly quantitative) (Found: C, 70·0; H, 5·4; N, 17·8. $C_{14}H_{13}ON_3$ requires C, 70·3; H, 5·43; N, 17·56%). It is easily soluble in ether, alcohol, chloroform, or ethyl acetate. When boiled with moderately dilute hydrochloric acid, it yields phenylacetaldehyde (which is partly oxidised to the acid), hydroxylamine, and benzenediazonium chloride which, as it is formed, is converted into phenol.

(*b*) A solution of ethyl benzylacetoacetate (14·6 g.) in alcohol (120 c.c.) was mixed at −5° with a solution of diazotised aniline (1 mol.) and the requisite quantity of sodium acetate. The product, which separated as a pale red, viscous oil in quantitative yield after 16 hours, was hydrolysed by warming with 10% aqueous alcoholic caustic potash (3 mols.) for 30 minutes and the solution diluted, filtered, and acidified; the phenylpyruvic acid phenylhydrazone, which separated as an oil and solidified, melting at 161° after recrystallisation (Wislicenus, *Ber.*, 1887, **20**, 592). A solution of the hydrazone in alcohol and 80% acetic acid (equal vols.) was filtered at room temperature and treated with finely-powdered sodium nitrite (3 mols. in one lot); evolution of carbon dioxide occurred. After 30 minutes, when the addition of water to a sample ceased to precipitate any of the original acid, the solution was gradually diluted with cold water. The oxime, which separated in yellow needles (yield quantitative) was recrystallised from benzene–light petroleum; it melted at 144°, alone or mixed with the oxime obtained by method (*a*) (Found: C, 69·9; H, 5·6%).

The *phenylcarbamate*, obtained quantitatively in slender, glistening, orange-red prisms by keeping a mixture of the oxime (3 g.) and phenylcarbimide (1·5 g.) in dry ether (40 c.c.) at 0° for 3 hours, crystallised from acetone in large, scarlet prisms, m. p. 154° (Found: N, 15·8. $C_{21}H_{18}O_2N_4$ requires N, 15·6%). The *benzoyl* derivative, prepared from benzoyl chloride (1 mol.) and the potassium salt of the oxime (1 mol.) in ethereal solution, crystallised from acetone in large, elongated, ruby prisms, m. p. 144—145° (frothing).

p-*Tolueneazoallylformaldoxime.*—A solution of *p*-toluenediazonium

sulphate (6 g.) in a little ice-water was treated with crystalline sodium acetate (10 g.), followed by a chilled aqueous solution containing allylmalonic acid (4·24 g.) and sodium acetate (7·2 g.). The subsequent addition of nitrous acid and the other operations were carried out as described above under (*a*). The product crystallised from warm benzene in slender, yellow needles, m. p. 93° (shrinking at 90°), and also crystallised well from light petroleum or aqueous alcohol, but not from other solvents. Yield, 25% (Found: C, 65·0; H, 6·5; N, 20·9. $C_{11}H_{13}ON_3$ requires C, 65·0; H, 6·4; N, 20·7%).

Attempts to prepare benzeneazopropaldoxime from ethylmalonic acid by this method resulted only in the production of resinous, uncrystallisable material.

p-*Tolueneazobenzylformaldoxime from Phenylpyruvic Acid* p-*Tolylhydrazone.—Ethyl phenylpyruvate* p-*tolylhydrazone*, obtained in nearly quantitative yield from ethyl benzylacetoacetate and *p*-toluidine by the method used in preparing the corresponding phenylhydrazone, crystallises in glistening, orange prisms, m. p. 72° (Found: N, 9·5. $C_{18}H_{20}O_2N_2$ requires N, 9·46%). It is fairly soluble in cold alcohol, more soluble in cold acetone, and very soluble in hot benzene. On hydrolysis, *phenylpyruvic acid* p-*tolylhydrazone* was obtained, which crystallises from alcohol in slender, yellow, felted needles and from acetone in slender prisms, m. p. 158° (frothing). (Found: C, 71·4; H, 6·1. $C_{16}H_{16}O_2N_2$ requires C, 71·5; H, 6·0%).

A solution of this acid (10 g.) in 50 c.c. of 80% acetic acid and 150 c.c. of alcohol was treated with powdered sodium nitrite (3 mols.) and kept for 30 minutes, after which the product was isolated as described above under (*b*). Successive recrystallisations from benzene and from acetone–light petroleum gave the pure *oxime*, m. p. 144° (slight decomp.). Yield, over 80% (Found: C, 70·0; H, 6·1. $C_{15}H_{15}ON_3$ requires C, 70·1; H, 5·9%).

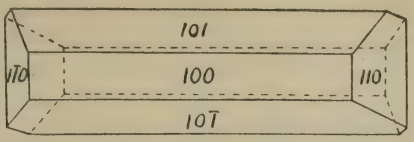
When light petroleum is added to a dilute solution of this oxime in acetone and the liquid allowed to evaporate slowly, the substance separates in transparent, orange-red crystals. Through the kindness of Sir Henry Miers, F.R.S., it has been possible to obtain measurements of these crystals, and the author takes this opportunity of thanking Mr. G. Greenwood, M.Sc., who kindly undertook the crystallographic examination. His report is as follows:—

Crystal symmetry: Monoclinic holohedral.

Axial constants: $a : b : c = 1{\cdot}352 : 1 : 1{\cdot}216$; $\beta = 83° 17'$.

Forms developed and Habit.—The crystals are usually elongated in the direction of the *b* axis and form prisms often 15 mm. long by

about 1·5 mm. thick (see Fig.). The forms present are {100}, {101}, {10$\bar{1}$}, and {110}.



Crystallographic angles.

Angle.	No. of measurements.	Limits.	Mean obs.	Mean calc.
(100) : (101)	11	44° 9′ —44° 30′	44° 20′	—
(100) : (110)	13	53° 9′ —53° 42′	53° 19′	—
(110) : (10$\bar{1}$)	10	67° 55′—68° 34′	68° 18′	—
(100) : (10$\bar{1}$)	17	51° 43′—52° 5′	51° 50′	51° 46′
(110) : (101)	9	64° 30′—65° 7′	64° 49′	64° 42′

The *phenylcarbamate*, obtained quantitatively by keeping a mixture of the oxime and phenylcarbimide (equal mols.) in much dry ether for 2 hours, is difficultly soluble in the usual organic media, but crystallises from much hot acetone in slender, vivid orange-red prisms, m. p. 152—153° (decomp.) (Found : N, 15·1. $C_{22}H_{20}O_2N_4$ requires N, 15·0%).

Benzeneazobenzaldoxime from Phenylglyoxylic Acid Phenylhydrazone.—Ethyl phenylglyoxalate phenylhydrazone was prepared by the general method described above and hydrolysed. The acid, m. p. 163°, obtained could not be converted into the oxime so smoothly as in the other two cases. It proved necessary to keep the mixture cold, avoid excess of sodium nitrite, and work up the product immediately Yield, about 25%.

This work arose out of a previous investigation undertaken at the suggestion of Prof. A. Lapworth, F.R.S., LL.D., to whom the author has pleasure in acknowledging his indebtedness. The author's thanks are also due to the Department of Scientific and Industrial Research for a grant in aid of the work.

The University, Manchester. [*Received, October 18th*, 1924.]

CCL.—*Angles of Contact and Polarity of Solid Surfaces.*

By Neil K. Adam and Gilbert Jessop.

From Dupré's equation

$$W = T_{SV} + T_{LV} - T_{SL} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which relates the free surface energies (surface tensions) at the interfaces of three phases S, V, L, with the work, W, done in separat-

ing S from L across the surface of separation, is combined with the equation of equilibrium of a liquid, L, resting on a solid surface, S, at an angle θ

$$T_{SV} - T_{SL} = T_{LV} \cos\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

we obtain

$$W = T_{LV} \ (1 + \cos\theta) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

thus eliminating the quantities T_{SL} and T_{SV} which cannot be determined. Equation (3) has been deduced by Pockels (*Physikal. Z.*, 1914, **15**, 39) and Edser (4th Report on Colloid Chemistry, 1922, p. 310), and an equivalent equation is deducible from Laplace's theory of capillarity (Poincaré, " Capillarité," 1895, 35). It appears to have been very little used. W being the adhesion of the liquid for the solid, and $2T_{LV}$ the cohesion of the liquid, equation (3) shows that zero angle of contact indicates an attraction of liquid for solid at least as great as that of liquid for liquid, 90° shows that this adhesion is half the cohesion of the liquid, and 180° would indicate no adhesion. Clearly measurements of angles of contact against water will give a quantitative measure of the polarity of a solid surface.

We have attempted to use the values of W for solid surfaces of long-chain aliphatic compounds as an indication of the orientation of the surface molecules. If many polar groups are at the free surface, the angle of contact should be low; if the surface consists solely of the hydrocarbon ends of the chains, the angle should be approximately the same as for paraffin wax.

In measuring the angle of contact, we have used a plate of the solid, held in an adjustable holder, which could be set at any angle with the surface, and also raised or lowered by rack and pinion. The water was contained in a glass vessel, preferably rectangular with plate glass sides, filled to the brim; the sides were several millimetres thick and were covered with paraffin on the top; the water surface was cleaned as necessary by scraping with strips of paraffined glass. The plate was set by trial at such an angle that the water surface remained horizontal right up to the edge of the plate, this being determined either by inspection from the side, or by observation of the reflexion of a source of light in the water surface very close to the plate. The angle between the plate and the water surface was then measured by a protractor.

These rather crude arrangements were adequate for this work, as the plates varied in angle of contact, in different parts, by several degrees; there would be little difficulty in improving the optical arrangements, but we would point out that it is of little use to employ accurate optical devices in the measurement of angle of contact

less both a proper means of obtaining a freshly cleaned water rface and a means of moving the plate relative to the water rface are provided. If contamination is present to an extent fficient to affect the surface tension of the water, the angle of ntact will be too low; the method of cleaning by *paraffined* rriers working on a fairly wide *paraffined* surface at the level the water has been exhaustively tested in recent work on thin ms and found simple and effective. Ablett's most accurate work paraffin wax (*Phil. Mag.*, 1923, **46**, 244) has probably given a good sult, although no means of frequently cleaning the surface was ailable, because paraffin wax practically does not contaminate water surface; nevertheless his apparatus would probably not satisfactory for the majority of substances. An ideal apparatus ight combine his method of rotating the cylinder of the solid th the method of cleaning by paraffined barriers.

The principal difficulty in measurement of contact angles is the ect of motion of the solid in dragging the liquid along with it. extreme cases, the angle when the liquid is advancing over the lid may be 60° greater than when it is receding. It is not necessary at there should be actual motion, for a force on the liquid tending move it has the same effect. The phenomenon is obvious on spection of a drop of water on a slightly dirty glass plate; it pears to have been first described in detail by Pockels (*loc. cit.*) d has been accurately measured in one case by Ablett. In the se of some surfaces, when the motion ceases, the line of contact liquid and solid slips back to give a true equilibrium contact gle, the same whether the motion was advancing or receding. is was only observed with one or two mechanically smooth surfaces, such as a scraped paraffin-wax surface. Ablett's results (n surfaces turned in a lathe) indicate that he obtained a true "stationary" angle of contact. In nearly all cases, including me with paraffin wax, when advancing motion ceased the liquid rse to an angle of contact which was greater than that to which fell after cessation of receding motion. The angle usually became nstant after motion, in less than a minute. So far as our servations go, it is indicated that the rougher the surface is, echanically, the greater is the difference between the advancig and receding angles; but it is not yet proved that there is ways a relation between mechanical roughness and the dragging ect.

The cause of this dragging effect (often called "hysteresis" of te angle of contact) seems to us to lie, not in any absorption of te liquid by the solid, but in a simple friction of the liquid on the rface. Let F be the force of friction which just prevents motion,

then, when the liquid is on the point of advancing, equation (3) becomes

$$T_{SV} - T_{SL} = T_{LV}\cos\theta_A + F \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and when just receding,

$$T_{SV} - T_{SL} = T_{LV}\cos\theta_R - F \quad . \quad . \quad . \quad . \quad . \quad (5)$$

θ_A and θ_R are the angles of contact when the force is just sufficient to move the liquid forwards or backwards, and are therefore the angles measured after moving the plate a short distance and waiting till the angle becomes constant after the motion has ceased.

For the calculation of W by equation (3) the equilibrium angle is required. By adding (4) and (5), and eliminating $T_{SV} - T_{SL}$ by (2),

$$2\cos\theta = \cos\theta_A + \cos\theta_R \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and when (as with the aliphatic substances here considered) the angles are between 45° and 135°, no error greater than 2° arises by substituting

$$2\theta = \theta_A + \theta_R \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

By raising the plate of solid vertically by means of the rack and pinion, and taking the mean of the angles after advancing and after receding motion, the following values of the equilibrium angle of contact have been measured. The error is probably of the order 5° in most cases; the angle for a scraped paraffin-wax surface is probably correct to 1°, and agrees with other published determinations.

Surface.	Angle of contact.	Work of adhesion in ergs per sq. cm.
Paraffin wax:		
Scraped surface	105°	54
Solidified in air	105	54
Solidified in contact with water	85 to 100	79·4 to 60·4
Octadecyl iodide:		
Solidified in air	100	60·4
Scraped	95	66·5
Pure hexadecyl alcohol:		
Solidified in air	95	66·5
Scraped surface	50 to 75	123 to 92
Crystal flake	85	79·4
Kahlbaum's "cetyl alcohol" (not crystalline)	20 to 50*	—
Palmitic, stearic, and eicosanic acids, also commercial "stearic":		
Solidified in air	100 to 105	60·4 to 54
Scraped	50 to 105	123 to 54
Crystal flake	95	66
Octadecylamine and eicosylamine hydrochlorides:		
Flakes	45	128

* The "cetyl" alcohol contaminated the water surface very quickly, and possibly the surface tension of the water was lowered sufficiently to render these angles decidedly too low.

There is a strong tendency for the surfaces which have solidified
om a melt, in air, to approach the value for paraffin wax. This
dicates that the normal orientation of molecules is with the paraffin
ains outwards.

Paraffin wax and octadecyl iodide, which contain no groups
ving a strong affinity for water, give practically the same angle
a surface cut from the interior as at the natural surface. The
bstances which contain polar groups at one end of the molecule,
ids and alcohols, give very varying results for surfaces cut from
e interior. These may be as low as 50°, or have practically the
me value as the natural surface. It is known from the *X*-ray
idies of Müller and Shearer that these substances crystallise in
kes, the unit of which is a layer 2 mols. thick, which has the polar
oups in the interior and the hydrocarbon chains outwards. A
t surface which runs parallel to the direction of these flakes in
e solid mass will expose very few, if any, polar groups; but one
right angles will expose the maximum number. Hence the
riation in the results.

An attempt was made to produce a surface of hexadecyl alcohol
ntaining a very high concentration of polar groups, by solidifying
te mass in contact with water, so that the layer of molecules nearest
te water might be oriented with polar groups outwards. This
as not successful, probably because this outermost layer sticks
ore closely to the water, to which it is attracted by polar groups,
an to the solid plate, to which it is attracted only by the smaller
traction between methyl groups; surfaces crystallised in contact
th water were of two kinds, some having a small angle of about
°, others giving about 100°. Frequently both types of surface
re present on the same mass. It was observed that the surface
th low angle of contact had a fine structure and did not flake off,
te appearance indicating that the crystal flakes were nearly per-
ndicular to the water; those with high angle easily flaked off,
owing that the crystal flakes were parallel to the water.

The table also indicates a tendency of the crystalline flakes
rmed from alcoholic or benzene solutions) to have a lower angle
contact than the mass solidified from the melt. The difference
perhaps too small to be trustworthy in the case of the alcohols
d acids, but the amine hydrochlorides (which could not be examined
er solidification from a melt, as they decompose on melting)
ve a very low angle of contact in the flakes. It is very probable,
m the similarity of constitution and of the appearance of the
kes, that these flakes have the same molecular structure as those
the acids and alcohols. Thus the very strongly polar groups
the interior *appear* to exercise an appreciable attraction on the

water over a distance equal to the length of an octadecyl chain-about 22 Å.U. Owing to the fact that a layer of closely packe hydrocarbon chains is undoubtedly permeable to water molecule this cannot be taken as a proof that the attraction of the interi polar groups does actually extend to a distance 22 Å.U., still retai ing a considerable fraction of its intensity. The interchange water between the internal polar groups and the exteri may result in something approaching chains of water molecul in among the hydrocarbon chains, and this would render the exteri surface polar. The flakes of these amine hydrochlorides, immerse in water for some hours, swell, and form a colloidal solutio eventually.

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CCLI.—*The Parachor and Chemical Constitution. Part II. Geometrical Isomerides.*

By SAMUEL SUGDEN and HENRY WHITTAKER.

WHILST many physical properties of geometrical isomerides hav been investigated and correlated with configuration, no systemati study of the surface tensions of such substances appears to have bee made. The work now described was commenced about two yea ago with the object of collecting data for pairs of isomerides c known configuration which might provide a basis for a method c determining configuration when the chemical evidence was nc conclusive. Meanwhile it was found by one of us (Sugden, J 1924, **125**, 1178) that the parachor, a quantity involving surfac tension and density, can be expressed as a simple additive functio of certain atomic and structural constants; from these constant it is possible to calculate the theoretical parachor for all the sul stances studied and, by comparison of this with the observed figur to detect the existence of any anomalies.

The determination of the parachor of geometrical isomerides i also of interest, since it has been found (Sugden, Reed, and Wilkin this vol., p. 1525) that by means of this constant a distinction ca be drawn between the two types of double bond which are predicte by the " octet " theory of valency as developed by Lewis, Langmui and Lowry. The non-polar double bond, consisting of two coval encies, adds 23·2 units to the parachor, whilst the semipolar doubl bond, which is made up of one covalency and one electrovalency lowers the molecular parachor by 1·6 units. It is therefore an eas

atter to determine experimentally the type of linking present in a rticular compound. Lowry has suggested that the "activated" olecule of an ethylene derivative may contain a semipolar double nd; this may not, of course, persist in the resting state and ngmuir (*loc. cit.*) assumes that carbon–carbon double bonds are n-polar, so that each carbon atom possesses a complete octet. rther it has been suggested by one of us (Sugden, J., 1923, **123**, 64), that there must be free rotation about a semipolar double nd; hence it would be expected that compounds which exhibit ometrical isomerism would possess a linking of the non-polar pe. It may be stated at once that all the ethylene derivatives so r examined, including those discussed in the present paper, have en found to contain non-polar double bonds.

The substances which have been measured are all methyl esters unsaturated acids. Esters were used to avoid the complication troduced by association of the free acids, and methyl esters were osen so that the loading of the molecule, which might obscure nall differences between isomeric substances, should be as small possible.

The results obtained are shown in the accompanying table. Since e calculated value of the parachor includes the effect of a non-olar double bond, the good agreement between the figures in the st two columns shows that all these compounds contain this type linking. If a semipolar double bond were present the molecular rachor would be 24·8 units lower, and whilst deviations of a few nits are present in the observed figures none of them is large enough suggest the occurrence of this type of bond.

Parachors of cis- *and* trans-*Unsaturated Esters.*

Methyl ester.	Configuration.	Authority.	Parachor. Obs.	Calc.
nnamate	trans	Liebermann [1]	373·9	377·9
*allo*Cinnamate	cis	,,	376·1	,,
Bromocinnamate	trans	Erlenmeyer [2]	426·6	428·8
Bromo*allo*cinnamate	cis	,,	427·9	,,
Bromocinnamate	trans	Michael and Brown [3]	424·8	,,
Bromo*allo*cinnamate	cis	,, ,,	427·5	,,
esaconate	trans	van't Hoff [4]	341·9	347·8
traconate	cis	,,	346·1	,,
umarate	trans	,,	308·5	308·8
aleate	cis	,,	309·6	,,

[1] *Ber.*, 1890, **23**, 2511. [2] *Ibid.*, p. 2130. [3] *Ibid.*, 1886, **19**, 1378. [4] "Die agerung der Atome im Raume," Braunschweig, 1877, 21.

There is a small but systematic difference between the values of ie parachor for each pair of isomerides; the *cis*-compounds, in hich two bulky groups are adjacent, give values for the parachor

closely approximating to the theoretical figure, whilst the *trans*-compounds give rather lower values. The difference is small and varies from one unit in the case of maleic and fumaric esters to four units for the mesaconic and citraconic esters. It is therefore little greater than the experimental error; but it appears systematically in each of the pairs of compounds examined, so that configuration does seem to have a real although small effect upon the molecular parachor.

Isomeric substances, *e.g.*, the esters of the formula $C_6H_{12}O_2$ and the three xylenes, have very nearly the same parachor (Sugden, *loc. cit.*, 1180, 1185). Since the atomic constants do not vary in different classes of substances, any differences between the parachors of isomerides must be due to marked differences in structure. The structural constants so far evaluated range from 46·6 for the triple bond to 6·1 for a six-membered ring and appear to depend chiefly upon the degree of unsaturation, or rather upon the crowding of the orbits of shared electrons. The semipolar double bond with a constant of −1·6 fits in with this conception, since, for example, in sulphates and phosphates there is no chemical evidence of unsaturation. Thus a marked difference between the parachors of isomerides would be expected to occur only with a marked difference in structure and in degree of unsaturation, as, for instance, in benzene, for which $[P]$ calc. = 207·1, and dipropargyl, for which $[P]$ calc. = 224·6. It is therefore not surprising that the configuration of geometrical isomerides has only a small influence upon the molecular parachor.

Experimental.

The isomerides of the cinnamic series were prepared by Sudborough's methods (J., 1903, **83**, 666, 1153). Cinnamic acid was converted into ethyl αβ-dibromo-β-phenylpropionate, the latter treated with alcoholic caustic potash, and the resulting mixture of α-bromocinnamic and α-bromo*allo*cinnamic acids separated by means of the barium salts. Phenylpropiolic acid was prepared by heating bromocinnamic acid with aqueous caustic potash. Sudborough recommends the use of a 20% solution of potash and gently heating on the water-bath, but a better conversion resulted by heating more vigorously with 30% potash. Even under these conditions the reaction was not complete, and difficulty was experienced in the purification of the phenylpropiolic acid until it was found that its barium salt was soluble in dilute ammonia and so could be readily separated from the insoluble barium bromocinnamate. The β-bromo-acids were prepared by the addition of phenylpropiolic acid to saturated aqueous hydrobromic acid, and the isomerides separated by means of their barium salts. *allo*Cinnamic acid was obtained

by reducing β-bromo*allo*cinnamic acid with zinc dust and 96% alcohol; the directions given by Michael (*Ber.*, 1901, **34**, 3651) for the preparation of *iso*cinnamic acid were followed, but the results confirmed the conclusions of Sudborough (*loc. cit.*) that the product is nearly pure *allo*cinnamic acid.

With one exception the methyl esters were prepared from the free acids by the Fischer-Speier method. Maleic acid under this treatment gave a mixture of fumarate and maleate which contained very little maleate; this ester was therefore made by the action of methyl iodide on the silver salt.

The surface tensions of the purified esters were determined by the method of maximum bubble pressure (J., 1922, **121**, 860; 1924, **125**, 27). Seven bubblers were used in the course of the work and in general each substance was measured on two instruments. The constants for these are tabulated below. The densities over a suitable temperature range were determined by means of the

App.	3b.	4a.	4c.	4d.	5b.	6.	6a.
r_2 cm.	0·159	0·139	0·139	0·139	0·140	0·156	0·156
A ...	0·004664	0·003708	0·004790	0·007767	0·009655	0·004439	0·009109

U-shaped pyknometer previously described (J., 1924, **125**, 1171). In the tables below, t is the corrected temperature, P the difference in pressure in dynes/cm.^{2} required to liberate bubbles from the two tubes, D the density in gm./c.c., ϕ the correction factor, and γ the surface tension in dynes/cm. The parachor is calculated by the formula $[P] = \gamma^{1/4}M/D$, where M is the molecular weight.

Methyl cinnamate was recrystallised from ligroin and melted sharply at 33·5° (corr.), M 162·1. Densities determined: 1·078 at 36°, 1·069 at 47°, 1·058 at 61°, 1·046 at 76°, 1·035 at 90°; whence $D_{4^\circ}^{t^\circ} = 1{\cdot}107 - 0{\cdot}000795\ t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
4a	46°	9926	1·070	1·010	37·17	374·1
4c	56	7373	1·062	1·0135	35·78	373·4
4a	67	9353	1·053	1·011	35·05	374·4
4c	75	6960	1·047	1·014	33·80	373·4
4a	90	8696	1·035	1·011	32·60	374·3
					Mean	373·9

This substance was measured by Walden and Swinne (*Z. physikal. Chem.*, 1912, **79**, 730) and by Morgan and Chazal (*J. Amer. Chem. Soc.*, 1913, **35**, 1821). They used the density data of Weger (*Annalen*, 1883, **221**, 75), which are 4% lower than ours. Calculated with the aid of our densities, the surface tensions found by Walden and Swinne agree well with our measurements, whilst those of Morgan and Chazal are still low. The latter workers give no criteria by which the purity of their specimen can be judged.

Methyl allo*cinnamate* boiled at 129—130° (corr.)/17 mm., *M* 162·1. Densities determined: 1·088 at 20°, 1·078 at 30°, 1·057 at 51°, 1·047 at 62°, 1·029 at 80°; whence $D_4^t = 1·107 - 0·000977\,t$.

App.	*t.*	*P.*	*D.*	ϕ.	γ.	Parachor.
4d	20°	5069	1·088	1·020	40·17	375·2
,,	41	4732	1·067	1·021	37·53	376·2
,,	62	4400	1·047	1·022	34·93	376·6
,,	78	4139	1·031	1·023	32·88	376·5
					Mean	376·1

Methyl α-*bromocinnamate* boiled at 165° (corr.)/16 mm., *M* 241·0. Densities determined: 1·475 at 20°, 1·450 at 40°, 1·419 at 65°, 1·388 at 90°, 1·363 at 110°, 1·333 at 135°; whence $D_4^t = 1·500 - 0·001238\,t$.

App.	*t.*	*P.*	*D.*	ϕ.	γ.	Parachor.
3b	20°	9618	1·475	1·0165	45·59	424·6
6	30	9828	1·463	1·016	44·32	425·0
3b	51	8810	1·436	1·0175	41·80	426·9
6	61	8966	1·424	1·017	40·47	427·0
3b	81	8044	1·399	1·019	38·22	428·4
4c	112	6948	1·361	1·018	33·87	427·3
,,	131	6469	1·337	1·0195	31·57	427·3
					Mean	426·6

Methyl α-*bromo*allo*cinnamate* boiled at 153·5—154° (corr.)/14 mm., *M* 241·0. Densities determined: 1·450 at 20°, 1·429 at 39°, 1·406 at 57°, 1·397 at 65°, 1·378 at 81°; whence $D_4^t = 1·475 - 0·001195\,t$.

App.	*t.*	*P.*	*D.*	ϕ.	γ.	Parachor.
3b	20°	9155	1·451	1·017	43·41	426·4
6	30	9380	1·439	1·016	42·30	427·3
3b	48	8468	1·417	1·018	40·20	427·4
6	60	8588	1·403	1·017	38·77	428·8
3b	81	7595	1·378	1·0195	36·10	428·8
					Mean	427·9

Methyl β-*bromocinnamate* boiled at 166·5° (corr.)/16 mm., *M* 241·0. Densities determined: 1·468 at 20°, 1·450 at 36°, 1·435 at 49°, 1·411 at 70°, 1·400 at 80°; whence $D_4^t = 1·490 - 0·00113\,t$.

App.	*t.*	*P.*	*D.*	ϕ.	γ.	Parachor.
3b	20°	9445	1·468	1·017	44·79	424·7
4c	32	8706	1·454	1·016	42·36	422·9
,,	53	8263	1·439	1·016	40·21	424·5
6	61	8855	1·421	1·017	39·96	426·5
4c	77	7699	1·404	1·017	37·49	425·0
					Mean	424·8

Methyl β-*bromo*allo*cinnamate* was recrystallised from ligroin and melted sharply at 59° (corr.), *M* 241·0. Densities determined: 1·386 at 62°, 1·376 at 70°, 1·358 at 85°, 1·346 at 95°; whence $D_4^t = 1·461 - 0·00121\,t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
6a	66°	3814	1·381	1·038	36·04	427·7
4a	71	9372	1·375	1·014	35·23	427·1
,,	81	9064	1·363	1·014	34·07	427·3
6a	86	3537	1·357	1·041	33·54	427·5
4a	94	8690	1·347	1·015	32·70	427·9
					Mean	427·5

Dimethyl mesaconate boiled at 100° (corr.)/16 mm., M 158·1. Densities determined: 1·126 at 20°, 1·115 at 30°, 1·098 at 45°, 1·076 at 65°, 1·060 at 80°; whence $D_4^t = 1·148 - 0·00110t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
6a	20°	3691	1·126	1·032	34·68	340·8
4a	32	9010	1·113	1·012	33·80	342·6
6a	52	3268	1·091	1·035	30·80	341·5
4a	63	7945	1·079	1·013	29·84	342·5
6a	80	2928	1·060	1·038	27·68	342·2
					Mean	341·9

Dimethyl citraconate boiled at 103·5° (corr.)/16 mm., M 158·1. Densities determined: 1·113 at 26°, 1·101 at 36°, 1·091 at 45°, 1·081 at 55°, 1·070 at 65°, 1·056 at 78°; whence $D_4^t = 1·140 - 0·00108\,t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
6a	20°	3801	1·119	1·031	35·69	345·5
4a	32	9208	1·106	1·011	34·51	346·6
6a	53	3332	1·083	1·034	31·37	345·6
4a	64	8203	1·071	1·012	30·78	347·7
6a	79	2986	1·055	1·037	28·20	345·3
					Mean	346·1

Dimethyl fumarate, recrystallised from ligroin, melted sharply at 102° (corr.), M 144·1. Densities determined: 1·049 at 106°, 1·032 at 121°, 1·022 at 129°, 1·010 at 140°, 0·999 at 150°, 0·987 at 160°; whence $D_4^t = 1·170 - 0·00114\,t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
6a	106°	2708	1·049	1·041	25·67	309·3
,,	123	2503	1·029	1·043	23·77	309·3
4a	132	6040	1·019	1·016	22·75	308·9
6a	146	2221	1·003	1·048	21·20	308·4
4a	163	5083	0·984	1·018	19·18	306·6
					Mean	308·5

Dimethyl maleate boiled at 102° (corr.)/17 mm., M 144·1. Densities determined: 1·160 at 20°, 1·144 at 35°, 1·115 at 60°, 1·075 at 95°, 1·058 at 113°, 1·031 at 135°; whence $D_4^t = 1·183 - 0·00112\,t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
4c	24°	7682	1·156	1·014	37·31	308·4
5b	35	3642	1·144	1·030	36·21	309·0
4c	51	7020	1·126	1·015	34·12	309·3
5b	67	3239	1·108	1·032	32·26	310·1
4c	86	6150	1·087	1·017	29·95	310·1
,,	113	5509	1·056	1·018	26·85	310·0
,,	143	4795	1·023	1·020	23·42	310·0
					Mean	309·6

Summary.

(1) The surface tension and the density of five pairs of geometrical isomerides have been measured over a range of temperatures.

(2) All the substances examined contain a non-polar double bond adding 23·2 units to the molecular parachor.

(3) The *cis*-compounds, in which two bulky groups are adjacent, have slightly higher parachors than the corresponding *trans*-compounds.

One of us (S. S.) wishes to express his thanks to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the cost of this investigation.

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FETTER LANE, E.C. 4. [*Received, July 9th*, 1925].

CCLII.—*A New Synthesis of Aldehydes.*

By HENRY STEPHEN.

THE basis of this new method is the conversion of a nitrile through the imino-chloride (which need not be isolated) into an aldehyde with the same number of carbon atoms. The most suitable reducing agent is anhydrous stannous chloride * dissolved in ether saturated with hydrogen chloride. Finely powdered, anhydrous stannous chloride (1½ mols.) is suspended in dry ether, which is then saturated with dry hydrogen chloride until the mixture separates into two layers, the lower viscous layer consisting of stannous chloride dissolved in ethereal hydrogen chloride. The nitrile (1 mol.) is now added with vigorous shaking and, after a few minutes, separation begins of a white, crystalline aldimine stannichloride,

$$(R{\cdot}CH{:}NH,HCl)_2,SnCl_4.$$

The course of the formation and reduction of the imino-chloride is therefore as follows: $R{\cdot}CN + HCl \longrightarrow R{\cdot}CCl{:}NH$; $R{\cdot}CCl{:}NH + SnCl_2 + 2HCl \longrightarrow R{\cdot}CH{:}NH,HCl + SnCl_4$. After removal of this

* The anhydrous stannous chloride for these reactions was prepared by heating the crystalline variety until the temperature reached 180°. The product contained some stannous oxide, but this appears to be insoluble in ether saturated with hydrogen chloride. A convenient and rapid method for preparing pure anhydrous stannous chloride is to dissolve the fused mass obtained as above in pyridine. Solution takes place with evolution of heat and the insoluble stannous oxide is then filtered off. The filtrate deposits fine, white needles of a *double* compound, $SnCl_2,2C_5H_5N$ (Found: $SnCl_2$, 53·2; C_5H_5N, 46·4. $SnCl_2,2C_5H_5N$ requires $SnCl_2$, 53·2; C_5H_5N, 46·8%). When the double compound is heated under diminished pressure the pyridine is removed; the residue is anhydrous stannous chloride.

salt the ether may be again employed for another preparation. The salt is readily hydrolysed by warm water, and the aldehyde formed may be removed by distillation with steam or extraction with a solvent.

The method is applicable to aliphatic and aromatic nitriles, and the yields are usually almost quantitative. As the rate of deposition of the stannichloride varies in different cases, it is advantageous to allow at least two hours for completion of the reaction.

3 : 4 : 5-Trimethoxybenzonitrile and other nitriles which are only sparingly soluble in cold ether may be dissolved in chloroform and the solution added to the reducing agent.

o-Toluonitrile and α-naphthonitrile give only small yields of the respective aldehydes. This is no doubt due to steric hindrance, of which the two nitriles form well-known examples; both, for instance, fail to give imino-ethers (Pinner, " Die Imidoäther und ihre Derivate," 1892, pp. 4, 81), for the formation of which an imino-chloride is essential.

A special application of the method is the formation of indole by reduction of *o*-nitrophenylacetonitrile; sufficient reducing agent is employed to reduce both the imino-chloride and the nitro-group :

$$C_6H_4\langle\begin{matrix}CH_2\cdot CN\\NO_2\end{matrix} \rightarrow C_6H_4\langle\begin{matrix}CH_2\cdot CHO\\NH_2\end{matrix} \rightarrow C_6H_4\langle\begin{matrix}CH\\NH\end{matrix}\rangle CH$$

(compare Pschorr, *Ber.*, 1910, **43**, 2543).

Experimental.

n-*Octaldehyde*.—Octonitrile was prepared by warming a solution of octoamide in thionyl chloride on the water-bath for 30 minutes and removing the excess of thionyl chloride under diminished pressure. The residue of nitrile (b. p. 87°/10 mm.) was almost pure and the yield quantitative. The method has been applied to the amides of myristic, palmitic, and stearic acids with equally good results.

Octonitrile (25 g.) was brought into reaction with stannous chloride (57 g.) in dry ether (200 c.c.), saturated with hydrogen chloride as described above. The aldehyde produced by hydrolysis of the stannichloride was isolated by distillation with steam and extraction with ether. It was obtained as a colourless oil, b. p. 65°/11 mm., having a strong lemon-like odour. Prepared by the usual methods and crystallised from methyl alcohol, the oxime was obtained in fine, silky needles, m. p. 60°, the semicarbazone in needles, m. p. 98°, and the *p-nitrophenylhydrazone* in bright yellow needles, m. p. 80° (Found : N, 15·8. $C_{14}H_{21}O_2N_3$ requires N, 15·9%).

Myristaldehyde was prepared from the corresponding nitrile, but being only slightly volatile in steam it was extracted with warm ether after hydrolysis of the stannichloride. It was obtained as thin, colourless laminæ, m. p. 23°, b. p. 155°/10 mm., and rapidly polymerised to a white solid, m. p. 65°. The oxime and semicarbazone crystallised from methyl alcohol in needles, m. p. 82·5° and 106·5°, respectively (compare Le Sueur, J., 1905, **87**, 1900). The p-*nitrophenylhydrazone* is a bright yellow, crystalline powder, m. p. 95° (Found: N, 12·4. $C_{20}H_{33}O_2N_3$ requires N, 12·1%).

Palmitaldehyde formed thin plates with nacreous lustre (from ether), m. p. 34°; the polymeride had m. p. 73—74°. The oxime and semicarbazone crystallised from methyl alcohol in needles, m. p. 88° and 107°, respectively (Le Sueur, *loc. cit.*). The p-*nitrophenylhydrazone* formed yellow needles, m. p. 96·5°, from alcohol (Found: N, 11·3. $C_{22}H_{37}O_2N_3$ requires N, 11·2%).

Stearaldehyde has m. p. 38°, not 63·5° as stated by Krafft (*Ber.*, 1880, **13**, 1417). It rapidly polymerises to a white solid, m. p. 80° The oxime and semicarbazone crystallise in needles, m. p. 89° and 108—109°, respectively. The p-*nitrophenylhydrazone* forms yellow needles, m. p. 101°, from methyl alcohol (Found: N, 10·6. $C_{24}H_{41}O_2N_3$ requires N, 10·4%).

Benzaldehyde.—Benzonitrile is rapidly and almost quantitatively converted into benzaldehyde by the new method. The *stannichloride* was obtained in white needles from alcohol (Found: Sn, 21·2. $C_{14}H_{16}N_2Cl_6Sn$ requires Sn, 21·8%). The salt, if dry, may be preserved indefinitely. It dissolves in water, but is rapidly hydrolysed when the solution is warmed.

3 : 4 : 5-*Trimethoxybenzaldehyde.*—The corresponding nitrile is readily obtained by the action of thionyl chloride on the amide (yield 90%), and without further purification melts at 93° as stated by Harding (J., 1911, **99**, 1594). A solution of the nitrile (9 g.) in 20 c.c. of chloroform is added to anhydrous stannous chloride (9 g.) in ether (150 c.c.) saturated with hydrogen chloride. After an hour the yellow stannichloride is filtered off, hydrolysed by boiling water, and the solution filtered. 3 : 4 : 5-Trimethoxybenzaldehyde crystallises from the filtrate in shimmering leaves, m. p. 74—75°. The oxime has m. p. 88°; the semicarbazone, m. p. 218°; and the *p*-nitrophenylhydrazone, m. p. 201° (compare Mauthner, *Ber.*, 1908, **41**, 923).

Indole.—*o*-Nitrophenylacetonitrile (3 g.) is added to a solution of anhydrous stannous chloride (16 g.) in ether (100 c.c.) saturated with hydrogen chloride. After remaining 2 hours, the stannichloride is filtered off, dissolved in water, the solution made alkaline with sodium hydroxide. and the indole removed in a current of

steam. The product, m. p. 52° (yield 1·2 g.), shows all the characteristic properties of indole.

The following aldehydes have been prepared by the new method, and except in the cases marked * the yields were almost quantitative. *o*-Tolualdehyde,* b. p. 94°/10 mm.; p-*nitrophenylhydrazone*, red needles, m. p. 222°, from alcohol (Found: N, 16·2. $C_{14}H_{13}O_2N_3$ requires N, 16.4%). *p*-Tolualdehyde, b. p. 106°/10 mm.; p-*nitrophenylhydrazone*, similar to the above, m. p. 200·5° (Found: N, 16·5%). *o*- and *p*-Chlorobenzaldehydes, phenyl-, *p*-chlorophenyl-, and *p*-tolyl-acetaldehydes (p-*nitrophenylhydrazone* of the last, yellow needles from alcohol, m. p. 144·5°. Found: N, 15·3. $C_{15}H_{15}O_2N_3$ requires N, 15·6%), cinnamaldehyde and β-phenylpropaldehyde, α-naphthaldehyde * (m. p. 33—34°; oxime, m. p. 39°; semicarbazone, m. p. 222°; p-*nitrophenylhydrazone*, orange needles, m. p. 234°. Found: N, 14·4. $C_{17}H_{13}O_2N_3$ requires N, 14·4%). The investigation is being continued.

In conclusion, the author has to thank Professors Lapworth and Robinson for their interest in the research.

THE UNIVERSITY, MANCHESTER. [*Received, June 26th*, 1925.]

CCLIII.—*ββ′-Dichloro- and ββ′-Dibromo-diethyl Selenides and their Simple Halogen Derivatives.*

By HUGH CHESTER BELL and CHARLES STANLEY GIBSON.

IN studying the reaction between ethylene and selenium monochloride, Bausor, Gibson, and Pope (J., 1920, **117**, 1453) showed that ββ′-dichlorodiethyl selenide dichloride (m. p. 122·5°) is formed and that the reaction proceeds according to the equation $2CH_2{:}CH_2 + 2Se_2Cl_2 = (CH_2Cl{\cdot}CH_2)_2SeCl_2 + 3Se$. Heath and Semon (*Ind. Eng. Chem.*, 1920, **12**, 1100) suggested that the final product is *s*-tetrachlorodiethyl selenide, $(CHCl_2{\cdot}CH_2)_2Se$, m. p. 118°.† On the other hand, Boord and Cope (*J. Amer. Chem. Soc.*, 1922, **44**, 395) agree that the final product is ββ′-dichlorodiethyl selenide dichloride, but they advance arguments to prove that the reaction goes in two stages:

(*a*) $2C_2H_4 + Se_2Cl_2 = (C_2H_4Cl)_2Se + Se$.
(*b*) $(C_2H_4Cl)_2Se + Se_2Cl_2 = (C_2H_4Cl)_2SeCl_2 + 2Se$.

In their paper Boord and Cope do not give any indication that they have investigated the reaction between ethylene and selenium

† These authors state that hydrogen chloride is evolved during the reaction. We have found that this is not so if precautions are taken to exclude moisture.

monochloride and did not isolate ββ′-dichlorodiethyl selenide which, the present work has further proved, was described by Bausor, Gibson, and Pope for the first time (compare Boord, *Ind. Eng. Chem.*, 1919, **11**, 101). The argument advanced by Boord and Cope is based on the results of experiments on the reaction between selenium monochloride and propylene, butylene, and amylene, respectively, and they show in each case that when selenium monochloride is added to the olefine the ββ′-dichlorodialkyl selenide is produced (reaction *a*). The only case of the formation of a selenide dichloride found by Boord and Cope was when they carried out the reaction between selenium monochloride and propylene, substantially under the conditions maintained by Bausor, Gibson, and Pope in the case of ethylene, and they obtained ββ′-dichlorodipropyl selenide dichloride. If the reaction between the olefines and selenium monochloride is a general one and occurs in two stages as stated by Boord and Cope, then that between the selenide and selenium monochloride (*b*) must be quantitative and proceed under the ordinary conditions of the experiment. In only one case apparently did the authors try this; they found that when equimolecular quantities of selenium monochloride and ββ′-dichlorodibutyl selenide were mixed the selenide dichloride was not obtained. The work of Boord and Cope indicates that the selenide dichlorides from butylene and amylene are difficult to prepare and may not have been obtained, but it affords little evidence that the reaction between ethylene and selenium monochloride takes place in two stages.

When selenium monochloride in chloroform is added to a chloroform solution of ββ′-dichlorodiethyl selenide at the ordinary temperature the formation of ββ′-dichlorodiethyl selenide dichloride is, we find, instantaneous and selenium separates at once. Although it may be convenient to regard the formation of the selenide as a phase in the reaction, it is clear that it cannot exist in the presence of selenium monochloride for any appreciable time. We describe below a highly satisfactory method for the preparation of ββ′-dichlorodiethyl selenide from the dichloride in which the possibility of its contamination with selenium is avoided and since the preparation of the dichloride can be carried out so readily we have not investigated the possibility of the preparation of the somewhat toxic selenide directly from selenium monochloride which, at the best, would involve the separation of the product from selenium.

ββ′-Dichlorodiethyl selenide dichloride can be prepared not only by the action of ethylene on selenium monochloride, but also in quantitative yield from selenium tetrachloride,

$$2C_2H_4+SeCl_4=(CH_2Cl\cdot CH_2)_2SeCl_2,$$

and the separation of the product from selenium is thereby avoided. It is possible to chlorinate selenium in the presence of benzene (very little chlorination of the latter takes place) or other suitable solvents to the tetrachloride and to convert this quantitatively into the final product, the same vessel being used throughout. In an analogous manner, ββ′-*dibromodiethyl selenide dibromide* is obtained, starting with selenium.

Bausor, Gibson, and Pope suggested that the colourless, crystalline substance, m. p. 23—25°, obtained in small quantity by reducing a cold aqueous solution of ββ′-dichlorodiethyl selenide dichloride with sulphur dioxide is probably ββ′-dichlorodiethyl selenide (*loc. cit.*). This is the fact. It can also be prepared by reducing the dichloride with hydrogen sulphide or, best, with potassium metabisulphite. It has a characteristic and persistent garlic-like odour and its toxicity appears to be very much less than that of ββ′-dichlorodiethyl sulphide. The corresponding ββ′-*dibromodiethyl selenide* is prepared in an analogous manner by reduction of the corresponding dibromide.

On treatment under appropriate conditions with either chlorine or bromine, the selenides combine with two atomic props. of the halogen. Apart from the dichloride and the dibromide already mentioned, we have prepared in this way ββ′-*dichlorodiethyl selenide dibromide* and ββ′-*dibromodiethyl selenide dichloride*. Since chlorine combines with ββ′-dichlorodiethyl selenide to give the product obtained by the reaction of ethylene with selenium monochloride, these compounds afford additional evidence of the correctness of the constitution given to ββ′-dichlorodiethyl selenide dichloride by Bausor, Gibson, and Pope. ββ′-Dichlorodiethyl selenide dichloride is precipitated from its aqueous solution by hydrochloric acid, and similarly the corresponding dibromide is precipitated by hydrobromic acid. The product obtained by adding hydrochloric acid to an aqueous solution of ββ′-dibromodiethyl selenide dibromide was proved to be the dichloride by its yielding ββ′-dibromodiethyl selenide on reduction with potassium metabisulphite. Under similar conditions, ββ′-dichlorodiethyl selenide dibromide is converted into ββ′-dichlorodiethyl selenide. It is interesting to compare the instability of ββ′-dichlorodiethyl sulphide dibromide (Gibson and Pope, J., 1920, **117**, 277) with the great stability of the analogous compounds of selenium now described.*

* Propylene reacts with selenium tetrachloride in a precisely similar manner to ethylene, and a quantitative yield of ββ′-dichlorodipropyl selenide dichloride results. This compound, reduced by potassium metabisulphite, is converted quantitatively into ββ′-dichlorodipropyl selenide (compare Boord and Cope, *loc. cit.*).

So far, all attempts to prepare direct oxidation products of ββ′-dichlorodiethyl selenide have failed. Although part of it is destroyed in the process, ββ′-dichlorodiethyl selenide dichloride can be recrystallised from concentrated nitric acid. Under the conditions for converting ββ′-dichlorodiethyl sulphide into the corresponding sulphoxide (Gibson and Pope, *loc. cit.*), ββ′-dichlorodiethyl selenide is partly destroyed and the dichloride crystallises out from the solution. Although the dichloride in aqueous solution behaves like the chloride of a bivalent metal, we have not been able to isolate either the corresponding hydroxide or oxide. An attempt to prepare the oxide by the action of ethylene on selenium oxychloride resulted in the formation of the dichloride and selenium dioxide, the following reaction presumably taking place :

$$2SeOCl_2+2C_2H_4=SeO_2+(C_2H_4Cl)_2SeCl_2.$$

Experimental.

ββ′-Dichlorodiethyl Selenide Dichloride.—Some quantity of this compound was prepared by the original method from selenium monochloride and the previous results were confirmed in all respects. When an excess of dry ethylene was passed into a dry benzene solution of selenium monochloride, hydrogen chloride was not evolved for the issuing gas produced no change in the alkalinity of standard sodium hydroxide. In an actual experiment, dry ethylene was passed into a rapidly stirred solution of 42 g. of selenium monochloride in dry benzene, cooled in running water. The yields of ββ′-dichlorodiethyl selenide dichloride and of precipitated selenium obtained were 24 g. and 19 g., respectively; according to the equation, they should be 25·4 g. and 21·7 g.

The preparation from selenium tetrachloride is, however, much more convenient, since all contamination with selenium is avoided. A rapid stream of chlorine is passed into a cooled, well-stirred suspension of finely divided selenium (1 part) in a convenient amount of benzene (carbon tetrachloride, chloroform or ether may be used). Selenium tetrachloride is formed with evolution of heat and separates rapidly as a pale yellow powder. The chlorine supply is then cut off, finely divided selenium (3 parts) added, and stirring continued for some time, during which the selenium tetrachloride is converted into the monochloride and almost complete solution is effected. The somewhat diluted benzene solution is filtered in a dry atmosphere, and chlorination is continued rapidly under the same conditions as before until the solution is completely decolorised and the selenium tetrachloride separates as a pale yellow powder, almost insoluble in most organic solvents. After

freeing the solution from excess of chlorine by passing dry air, ethylene is passed in until complete solution of the selenium tetrachloride is effected in the warm solvent, which should become quite colourless when the reaction is finished. The dichloride crystallises as the solution cools and the small amount remaining in solution can be recovered in the usual manner. In this way, from a total amount of 20 g. of selenium, 60—65 g. of ββ′-dichlorodiethyl selenide dichloride can be prepared conveniently in the course of about 8 hours including the preparation of the necessary ethylene. That the reaction between selenium tetrachloride and ethylene takes place according to the equation $2C_2H_4+SeCl_4=(C_2H_4Cl)_2SeCl_2$ was proved by passing ethylene into dry benzene in which 10 g. of the tetrachloride was suspended. Twelve grams of the resulting compound was obtained (theory requires 12·5 g.).

The identity of the compound prepared from selenium tetrachloride with that prepared from the monochloride was proved by its melting point (122·5°), by its crystalline form, and by its behaviour with sodium hydroxide in cold aqueous solution (Found : titratable Cl, 25·9; *M*, cryoscopic in hexachloroethane,* 276. Calc. for $C_4H_8Cl_4Se$: titratable Cl, 25·6%; *M*, 277·2). The compound is best purified by recrystallisation from chloroform. It can be almost quantitatively recovered from its aqueous solution by addition of concentrated hydrochloric acid and this is also a convenient method of purification. Its aqueous solution decomposes above 35°, and rapidly when boiled, with evolution of ethylene.

When concentrated hydrobromic acid was added to a cold aqueous solution of ββ′-dichlorodiethyl selenide dichloride, a yellow, crystalline precipitate was obtained which, after recrystallisation from chloroform, had m. p. 117° (decomp.) and was proved by its constants and by analysis to be *ββ′-dichlorodiethyl selenide dibromide*, obtained also in another way (see p. 1883).

In attempts to isolate ββ′-dichlorodiethyl selenide dihydroxide, careful addition of sodium hydroxide (2 equivs.) to the aqueous solution of the dichloride gave negative results. Similarly, in attempting to prepare ββ′-dichlorodiethyl selenide oxide by the action of dry silver oxide on a benzene solution of the dichloride, selenium was deposited and no oxide-like substance could be isolated.

ββ′-Dibromodiethyl Selenide Dibromide, $(CH_2Br{\cdot}CH_2)_2SeBr_2$, is prepared in an analogous manner to the dichloride. Finely divided selenium is suspended in pure carbon tetrachloride and bromine is added to the rapidly stirred suspension until the whole of the

* The use of hexachloroethane for the determination of molecular weights has not yet been described but, as soon as its general applicability has been determined, an account will be submitted for publication.

bromine is converted into the tetrabromide. The excess of bromine is removed either by boiling or by passing a current of dry air. Dry ethylene is then passed into the rapidly stirred suspension of the tetrabromide until the solution becomes clear; the ββ′-dibromodiethyl selenide dibromide dissolves in the warm solvent and crystallises on cooling. One crystallisation from chloroform is sufficient for complete purification, well-formed, bright yellow prisms, m. p. 118°, being obtained (Found : Br, 71·1. $C_4H_8Br_4Se$ requires Br, 71·6%).

ββ′-*Dichlorodiethyl Selenide*, $(CH_2Cl{\cdot}CH_2)_2Se$.—The substance, m. p. 23—25°, originally prepared by Bausor, Gibson, and Pope (*loc. cit.*) by passing sulphur dioxide into a cold aqueous solution of ββ′-dichlorodiethyl selenide dichloride, was prepared again by the same method and proved to be ββ′-dichlorodiethyl selenide identical with the product obtained more conveniently by a slightly different procedure.

ββ′-Dichlorodiethyl selenide dichloride may be reduced in boiling benzene solution by dry hydrogen sulphide. Sulphur separates and the reaction is finished when hydrogen chloride ceases to be evolved. On distilling off the benzene from the filtered solution, a product is obtained, m. p. about 24°, which is extremely difficult to obtain free from adhering sulphur. On extraction with dry ether, some sulphur is left undissolved, but the melting point of the product is scarcely affected. Fractional freezing of the material to free it from sulphur is not very satisfactory and even after repeating this process several times analysis shows that the resulting material is not quite pure (Found : Cl, 33·2%).

After many experiments the following method was finally adopted for preparing ββ′-dichlorodiethyl selenide conveniently in a state of purity. A solution of pure ββ′-dichlorodiethyl selenide dichloride (10—15 g.) in cold water is shaken with cold aqueous potassium metabisulphite (calc. quantity) and at once extracted with ether. The ethereal solution is washed with water, dried with calcium chloride, and evaporated; the selenide crystallises easily (yield almost theoretical). It is convenient to purify it by pressing on to clean unglazed porcelain and subsequent fractional freezing. It crystallises in colourless needles, m. p. 24·2° (Found : Cl, 34·7; Se, 38·6; *M*, cryoscopic in benzene, 196. Calc. for $C_4H_8Cl_2Se$: Cl, 34·4; Se, 38·4% : *M*, 206). Unlike the corresponding sulphide, it cannot be distilled in a water-pump vacuum without considerable decomposition. The distillate, however, contains some unchanged selenide which is identified by conversion into the dibromide (see below).

ββ′-Dichlorodiethyl selenide combines with chlorine (1 mol.) to

give the dichloride and with bromine (1 mol.) in chloroform solution. The reaction is quantitative: 0·3915 g. decolorised 0·315 g. bromine, the theoretical quantity being 0·303 g. bromine. The compound so formed is therefore ββ′-*dichlorodiethyl selenide dibromide*, $(C_2H_4Cl)_2SeBr_2$, which crystallises from chloroform in pale yellow prisms, m. p. 117° (decomp.). This compound, on reduction with potassium metabisulphite in the manner already described, yields ββ′-dichlorodiethyl selenide. It has been mentioned that when hydrobromic acid is added to a cold aqueous solution of ββ′-dichlorodiethyl selenide dichloride this dibromide is precipitated (see p. 1881) and the facts now brought forward prove that when ββ′-dichlorodiethyl selenide dichloride is dissolved in water the halogen atoms attached to the selenium are hydrolysed.

When a chloroform solution of selenium monochloride is added to a similar solution of ββ′-dichlorodiethyl selenide, selenium is at once precipitated and the filtered solution yields a quantitative amount of ββ′-dichlorodiethyl selenide dichloride. The reaction takes place with evolution of heat and proceeds according to the equation $Se_2Cl_2+(C_2H_4Cl)_2Se=(C_2H_4Cl)_2SeCl_2+2Se$.

When ββ′-dichlorodiethyl selenide is oxidised with nitric acid, the only product which has up to the present been isolated is ββ′-dichlorodiethyl selenide dichloride (identified by its melting point and crystalline form), part of the selenide being destroyed. An attempt to prepare the oxide by the action of ethylene on selenium oxychloride resulted in the formation of selenium dioxide and ββ′-dichlorodiethyl selenide dichloride, the selenium oxychloride reacting as an equimolecular mixture of selenium dioxide and selenium tetrachloride.

ββ′-*Dibromodiethyl Selenide*, $(CH_2Br{\cdot}CH_2)_2Se$.—This compound is prepared by reduction of ββ′-dibromodiethyl selenide dibromide by means of potassium metabisulphite under the conditions already described. It crystallises from ethyl alcohol in yellow needles, m. p. 44·2°, and is much more easily handled than the corresponding chloro-compound (Found: Br, 53·5. $C_4H_8Br_2Se$ requires Br, 54·2%).

It combines with chlorine in chloroform solution to give ββ′-*dibromodiethyl selenide dichloride*, $(C_2H_4Br)_2SeCl_2$, pale yellow prisms, m. p. 98—99°, from chloroform (Found: Cl+Br, 62·8. $C_4H_8Cl_2Br_2Se$ requires Cl+Br, 63·0%). This compound has a greater solubility in organic solvents than the analogous compounds already mentioned. The same compound is precipitated by adding a concentrated solution of hydrochloric acid to a cold aqueous solution of ββ′-dibromodiethyl selenide dibromide, but it has to be separated from some unchanged dibromide which is precipitated with it. As was expected, the melting point of the

product so obtained was somewhat low (96°), but, on reduction, it gave ββ′-dibromodiethyl selenide identical with an authentic specimen.

Addendum.

The reaction between propylene and selenium tetrachloride has also been carried out. ββ′-Dichlorodipropyl selenide dichloride, m. p. 76·5° (Boord and Cope, *loc. cit.*, give 81°), was obtained in almost theoretical yield. It is conveniently purified by dissolving in cold water, in which it is readily soluble, and reprecipitating with hydrochloric acid (Found: Cl, 46·7; calc., Cl, 46·5%). When reduced with potassium metabisulphite under the usual conditions, it was converted into ββ′-dichlorodipropyl selenide, which has not yet been obtained crystalline (Found: Cl, 30·1; calc., Cl, 30·3%).

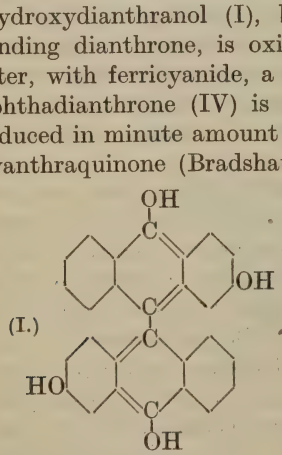
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LONDON, S.E. 1.

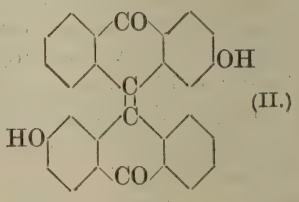
[*Received, July 13th*, 1925.]

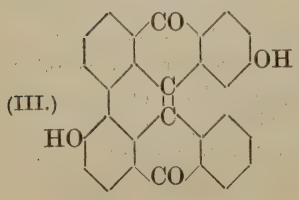
CCLIV.—*Reduction Products of the Hydroxyanthraquinones. Part VI.*

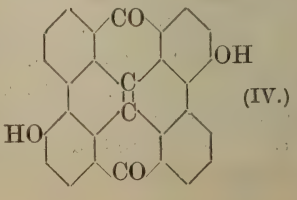
By ARTHUR GEORGE PERKIN and GEN YODA.

HALLER and PERKIN (J., 1924, **125**, 239) showed that when 3 : 6′-dihydroxydianthranol (I), but curiously enough not the corresponding dianthrone, is oxidised with alkaline permanganate or, better, with ferricyanide, a mixture of the helianthrone (III) and naphthadianthrone (IV) is obtained. These compounds are also produced in minute amount by the glucose–alkali fusion of 2-hydroxyanthraquinone (Bradshaw and Perkin, J., 1922, **121**, 913).









It appeared likely that the first product of the oxidation would be the dihydroxydianthraquinone (II) and it was actually found by Perkin and Haller (*loc. cit.*) that by the more gentle action of ferricyanide a product was obtained which seemed to consist of this substance in an impure condition. Experiment has now shown that this dihydroxydianthraquinone can be prepared in good yield by the action of iodine on a pyridine solution of tetra-acetyldihydroxydianthranol at about 80°, diacetoxydianthrone remaining unchanged under these conditions. This substance, apparently the first hydroxydianthraquinone to be prepared, consists of pale yellow leaflets, blackens about 280°, and does not appear to have a definite melting point. Though two formulæ are applicable to this compound, in which hydroxyls occupy either the 3 : 6′-* or 3 : 3′-positions, it evidently consists in the main of a single substance, because on oxidation with alkaline ferricyanide an excellent yield of the dihydroxyhelianthrone (III) is produced. On the other hand, whereas the melting point of the diacetyldianthraquinone, after crystallisation from acetic anhydride, is 293—295°, and this can be raised by repeated fractionation from tetrachloroethane to about 314—316° without apparent alteration in the character of the substance, it is possible that a small amount of a second variety is also produced. The melting points given of the dibenzoyl compound, 301—302°, and the dimethyl ether, 290—292°, vary to some extent with the rapidity of heating, but on the whole there is no definite evidence that the new dihydroxydianthraquinone consists of two isomerides. 3 : 3′-Dihydroxydianthraquinone (m. p. 293—295°) is easily reduced by zinc dust and ammonia to 3-hydroxyanthranol, but is unaffected by long treatment with sulphur dioxide in the presence of alcohol. By digestion with 3-hydroxyanthranol in boiling acetic acid solution 3 : 3′-dihydroxydianthrone is slowly produced, whereas acetyldihydroxydianthraquinone with chromic acid in the same solvent gives 2-acetoxyanthraquinone. Dihydroxydianthraquinone is more quickly affected by light than the corresponding helianthrone (*loc. cit.*), the pale yellow crystals rapidly becoming orange-coloured, evidently with production first of the latter compound; this change even occurs to some extent during crystallisation from much boiling acetone. Though the diacetyl and dimethyl compounds are less sensitive in the solid condition to light than the corresponding dihydroxy-derivative, after 5 weeks' exposure to light their

* Experiments in progress render it uncertain as to whether the dihydroxydianthranol reacts in these cases as the 3 : 6′-compound as was suggested (*loc. cit.*), but as the work is incomplete such formulæ are still employed for the present.

solutions in benzene had deposited diacetoxynaphthadianthrone and dimethoxynaphthadianthrone containing a little dimethoxyhelianthrone, respectively. It is thus evident that in these circumstances the helianthrone formation precedes that of the naphthadianthrone.

Experimental.

Tetra-acetyldihydroxydianthranol (0·5 g.) dissolved in pyridine (5 c.c.) was treated with a solution of iodine (0·5 g.) in pyridine (5 c.c.) and kept at 80° for 1½ hours. The reddish-brown liquid was poured into a freshly-acidified solution of sodium bisulphite, and the greenish-yellow precipitate collected and dried. On digestion with boiling acetic anhydride and pyridine for about ½ minute, crystals separated and when cold these were collected and recrystallised from much acetic anhydride. The acetyl compound thus produced became greenish-black at about 280°, melted at 293—295° (A), and was unaltered by further recrystallisation from the same solvent. On the other hand, by repeated crystallisation from tetrachloroethane or a mixture of this with acetic anhydride, the melting point rose to 314—316° (B) [Found: (A) C, 76·7; H, 4·2. (B) C, 76·6; H, 4·0; $CH_3 \cdot CO_2H$, 23·9. $C_{32}H_{20}O_6$ requires C, 76·8; H, 4·0; $CH_3 \cdot CO_2H$, 24·0%].

Owing to its sparing solubility in alcohol, the substance for the acetyl determination was dissolved in cold sulphuric acid overnight; the solution was then diluted with alcohol and treated in the usual manner. 3 : 6′-*Diacetoxydianthraquinone* forms small, pale yellow crystals sparingly soluble in the usual solvents, the solutions when hot possessing a green colour which fades on cooling; this property, also possessed by 3 : 6′-dihydroxydianthraquinone, appears to be characteristic of dianthraquinone derivatives. When diacetoxydianthraquinone (0·5 g.) in benzene (200 c.c.) was exposed to light for 5 weeks, it yielded an orange-brown, crystalline deposit (0·37 g.). This, on recrystallisation from nitrobenzene with the aid of animal charcoal, yielded pale yellow needles, melting above 350° and soluble in sulphuric acid with a red coloration, consisting evidently of diacetoxynaphthadianthrone (Found: C, 77·2; H, 3·4. $C_{32}H_{16}O_6$ requires C, 77·4; H, 3·3%).

As diacetoxydianthraquinone could not be satisfactorily hydrolysed with mineral acids, its suspension (1 g.) in boiling alcohol (25 c.c.) was treated with 10% caustic soda solution until all had dissolved. The solution was diluted with boiling water (25 c.c.) and immediately neutralised with hydrochloric acid; * pale yellow leaflets

* This operation must be carried out rapidly, otherwise discoloration is liable to occur.

then commenced to separate. After dilution with hot water (25 c.c.) and cooling, the crystals (yield 96% of theoretical) were collected and washed with a little acetone, which removed a trace of a red impurity (Found: C, 80·8; H, 4·0. $C_{28}H_{16}O_4$ requires C, 80·8; H, 3·8%).

Dihydroxydianthraquinone crystallises from pyridine and water in pale yellow plates which become black at about 280° and scarcely have a definite melting point. It is sparingly soluble in the usual solvents, but dissolves in alkalis with an orange-yellow colour which is fairly permanent in air. With sulphuric acid it gives a maroon-coloured liquid quickly passing to brownish-black and from this, after keeping, water precipitates a brown-black precipitate soluble in alkali with a similar colour. This is reduced by sodium hyposulphite to an orange-yellow liquid which quickly oxidises in air. The boiling ammoniacal solution is quickly decolorised by zinc dust, and on acidification deposits crystals, which give an acetyl compound, m. p. 158—159°, identical with 3-acetoxyanthranol. A solution of dihydroxyanthraquinone (0·2 g.) in absolute alcohol (160 c.c.) rapidly became orange-coloured in sunlight and after 6 weeks' exposure had deposited 0·1675 g. of crystals. These, after acetylation and fractional crystallisation of the product, gave 0·1 g. of diacetoxynaphthadianthrone, m. p. above 350°, and a little diacetoxyhelianthrone, m. p. 275—279°.

Dihydroxydianthraquinone is best kept in the dark, as the crystals become orange-coloured in a few hours, owing evidently to the action of light. Dihydroxydianthraquinone (1 g.) in water (25 c.c.) was dissolved by addition of 10% sodium hydroxide solution (3 c.c.), and 20% potassium ferricyanide (9 c.c.) slowly added in the cold. After 15 minutes, the mixture was acidified and the red precipitate collected (1·03 g.). This, after acetylation and recrystallisation of the product from benzene, gave 0·97 g. of diacetoxyhelianthrone, m. p. 277—279° (Found: C, 76·75; H, 3·6. Calc., C, 77·1; H, 3·6%).

Dibenzoyldihydroxydianthraquinone was obtained by heating dihydroxydianthraquinone (0·5 g.), benzoic anhydride (5 g.), and a trace of pyridine at 210° for 2 hours. Addition of alcohol to the partly cooled liquid caused the deposition of crystals, which were washed with an alcoholic solution of benzoic anhydride and finally with alcohol. The product was dissolved in much boiling benzene, the solution filtered and evaporated, when small, yellow plates separated, which darkened at 295° and melted at 301—302° to a green liquid (Found: C, 80·4; H, 3·8. $C_{44}H_{24}O_6$ requires C, 80·7; H, 3·8%).

Dimethoxydianthraquinone was prepared by treating the dihydr-

oxy-compound (1 g.) in methyl alcohol (30 c.c.) with equivalent amounts of methyl sulphate and methyl-alcoholic potash, until no colour change occurred on the addition of the latter. After dilution with hot water the crystals (0·85 g.) were collected, washed with cold alcohol, and dissolved in pyridine; the green solution was treated with a little sodium hydroxide, and hot water cautiously added. The crystals were collected and the latter operation, which has for its object the removal of a trace of incompletely methylated substance, was repeated. By recrystallisation from pyridine, the *dimethoxy*-derivative was obtained in small, rectangular, yellow plates which became green at about 270° and melted at 297—299°. On exposure to light it soon develops an orange colour (Found: C, 81·4; H, 4·5; CH_3, 6·7. $C_{30}H_{20}O_4$ requires C, 81·1; H, 4·5; CH_3, 6·75%).

When dimethoxydianthraquinone (1 g.) is dissolved in the necessary amount of boiling acetone in daylight (1300 c.c. approx.), and the solution evaporated to a small bulk, alteration occurs even during this short period and the crystalline deposit can be separated by fractionation from pyridine into (*a*) dimethoxydianthraquinone, m. p. 297—299°, and (*b*) a very sparingly soluble, orange compound (A), which did not melt at 320° dissolves in sulphuric acid with a red coloration and is probably dimethoxynaphthadianthrone. Again, a solution of dimethoxydianthraquinone (0·3 g.) in benzene (100 c.c.) on exposure to light became orange-coloured in about 30 minutes, and commenced to deposit an orange powder. This (0·128 g.), by crystallisation from nitrobenzene, was obtained in microscopic needles, which had not melted at 340° and were soluble in sulphuric acid with a red coloration. An analysis of the small amount of this compound available was unsatisfactory, but there can be little doubt that this and the compound A referred to above, which closely resembled it, consist of *dimethoxynaphthadianthrone*. The benzene filtrate on evaporation to dryness gave a dark-coloured residue which after solution in hot alcohol yielded yellow crystals; these, after purification, were soluble in sulphuric acid with a violet coloration and had the properties of dimethoxyhelianthrone.

CLOTHWORKERS RESEARCH LABORATORY,
THE UNIVERSITY, LEEDS. [*Received, June 17th,* 1925.]

CCLV.—*A Wandering of the Acetyl Group during Methylation.*

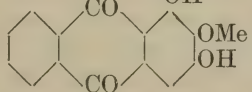
By Onro Kubota and Arthur George Perkin.

Oesch and Perkin (P., 1914, **30**, 213) submitted monoacetylalizarin (J., 1899, **75**, 433) to the action of diazomethane and after hydrolysis isolated from the product a small amount of alizarin 1-methyl ether (1) identical with that obtained from Chay root (J., 1893, **64**, 1160; 1907, **91**, 2068). Reinvestigation has now shown that, although the 1-methyl ether is always produced in this way, the main product is the 2-methyl ether. Careful examination of the monoacetylalizarin employed in these experiments indicated it to be a single substance, and indeed were this not the case it would be more likely to consist of a mixture of mono- and di-acetylalizarins than of the 1- and 2-acetyl derivatives.* The formation of alizarin 2-methyl ether in these experiments shows that whereas a small portion of the 2-acetylalizarin reacts normally with diazomethane, the acetyl group must wander from the 2- to the 1-position at some stage of the process, and the methyl then enters its place to give 2-methoxy-1-acetoxyanthraquinone; the yield of this is about 80% of the theoretical.

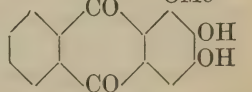
2 : 3-Diacetylanthragallol again, which can be readily obtained by the partial acetylation of anthragallol, on treatment with diazomethane gives as the main product a diacetylanthragallol monomethyl ether which evidently contains the methoxy-group in the 2-position, because the free substance (II), which crystallises in yellow needles, is soluble in dilute alkali with a red coloration similar to that given by purpuroxanthin. The more soluble fraction of the reaction product when hydrolysed gave a mixture from which, by means of the sparing solubility of its ammonium salt, the isomeric ether was isolated. This crystallises in orange-red needles, dissolves in alkali with a deep blue colour, and dyes mordanted calico shades of the alizarin type. It must therefore contain adjacent hydroxyls and is clearly anthragallol 1-methyl ether (III) (1-methoxyhystazarin), for if it were anthragallol



(I.)



(II.)



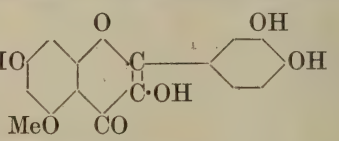
(III.)

* It is well known that in the anthraquinone series the 2-hydroxyl group is more readily acetylated than the 1-hydroxyl group (compare Dimroth, Friedemann, and Kämmerer, *Ber.*, 1920, **53**, 481).

3-methyl ether (3-methoxyalizarin) its formation would necessitate the respective wandering of the 2- and 3-acetyl groups into the 1- and 2-positions, or of the 3-acetyl group into the 1-position. It is unfortunate that a monoacetylanthragallol has not yet been obtained, for the action of diazomethane thereon should yield one or other of the anthragallol dimethyl ethers referred to above.

In a third series of experiments, tetra-acetylquercetin was employed, a substance which has been prepared by the action of acetic anhydride and sodium acetate on quercetin in the cold. This substance was originally thought (*loc. cit.*) to be the triacetyl derivative, but as a result of the present experiments only 3 : 7 : 3′ : 4′-tetra-acetylquercetin could be obtained. This acetyl derivative required more drastic treatment with diazomethane than was necessary in the case of the hydroxyanthraquinones, and in the product only one tetra-acetylquercetin monomethyl ether could be detected. The almost colourless, sparingly soluble quercetin monomethyl ether obtained by hydrolysis closely resembled, but is not identical with, the quercetin monomethyl ether, rhamnetin, previously studied (J., 1902, **81**, 469). By decomposition with alcoholic potash, it yielded phloroglucinol monomethyl ether, identified as its benzeneazo-compound, and there can be no doubt that this new quercetin methyl ether contains the methoxy-group in the 5-position adjacent to the carbonyl group (IV).

(IV.)



A wandering of the acetyl group does not occur in these circumstances. Interesting is the fact that this 5-methyl ether yields with alcoholic potassium acetate the salt $C_{16}H_{11}O_7K$, for, as quercetin gives a similar compound, it seems clear that the reactive hydroxyl, the position of which has not yet been determined with certainty, cannot be that situated in the 5-position. The wandering of an acetyl group has been observed by Wislicenus and Körner (*Ber.*, 1901, **84**, 218) in the case of the *o*-acetyl derivative of ethyl acetoacetate (compare also Claisen and Haase, *Ber.*, 1900, **33**, 3778), and numerous instances are known of its migration from hydroxyl to the amino-group (Auwers, *Annalen*, 1901, **332**, 159, etc.; Raiford and Couture, *J. Amer. Chem. Soc.*, 1922, **44**, 1792). Very interesting, again, is the work of Fischer, Bergmann, and Lipschitz (*Ber.*, 1918, **51**, 45), who showed that 3 : 4 : 5 : 3′ : 5′-penta-acetyl(para)-digallic acid, when hydrolysed, yields the 3 : 4 : 5 : 3′ : 4′-penta-hydroxy-*m*-digallic acid, a wandering of the galloyl nucleus from

the *p*- to the *m*-position occurring. Again, 3 : 5-diacetyl-4-benzoylgallic acid on hydrolysis in a similar manner yields not the *p*- but the *m*-benzoyl derivative, and a similar change has been observed in the case of 3-acetyl-4-benzoylprotocatechuic acid. Herzig and Tichatschek (*Ber.*, 1908, **39**, 268, 1557) have shown that under the influence of diazomethane the acetyl group in triacetylpyrogallol is partly replaced by methyl, whereas acetylphloroglucinol diethyl ether gives phloroglucinol methyl diethyl ether * in the same circumstances.

p-Acetoxybenzoic and *m*-hydroxybenzoic acids are mainly converted by diazomethane into the corresponding methoxybenzoic acids. The results of this investigation, however, differ † from the cases just mentioned in that the wandering of the acetyl group occurs during methylation itself, and though it was scarcely necessary to do so, this has been proved by an examination of the reaction products of each experiment. It is well known in the case of substances such, for instance, as β-resorcylic acid (J., 1895, **67**, 990), luteolin (J., 1900, **77**, 1316), and quercetin (J., 1913, **103**, 1632), all of which contain meta-hydroxyl, that on methylation with methyl iodide the methyl group in part, rather than substitute the hydrogen of the hydroxyl next to the carbonyl group, actually enters the ring. In the cases of 2-acetylalizarin and of 2 : 3-diacetylanthragallol, this cannot occur, and with 3 : 7 : 5′ : 4′-tetra-acetylquercetin this would appear to be prevented by the presence of the 3-acetyl group.

This curious interchange of methyl and acetyl is without doubt connected with the peculiar property of the hydroxyl adjacent to the carbonyl group,‡ and it has been suggested that this may be due to the existence of the ortho-quinonoid arrangement (V) (*loc. cit.*).



(V.) (VI.)

Dimroth and Faust (*Ber.*, 1921, **54**, 3020) presume that there is an unstable valency between the ketonic oxygen and the

* Experiment has shown that diacetylalizarin is not affected by treatment with diazomethane.

† On the other hand, when 2-acetylalizarin 1-methyl ether is hydrolysed with alcoholic ammonia or with hydrochloric acid the resulting free ether, which when pure is yellow, is always contaminated with a trace of red impurity which may be removed with baryta water. Although a wandering of the methyl group with formation of alizarin 2-methyl ether may be suspected, this is as yet uncertain.

‡ Or, as the result of the work of Fischer (*loc. cit.*), of that in the para-position thereto.

hydrogen of the 1-hydroxyl group, a view also taken by Sidgwick and Callow (J., 1924, **125**, 527), who suppose that a six-membered chelate ring (VI) exists in compounds of this type.

A grouping of this kind evidently does not exist, or is much weakened, when an acyl or an alkyl group is substituted for the hydrogen of the 1-hydroxyl group, since such substances possess the pale yellow colour characteristic of anthraquinone itself, and if this chelate ring is present, the ease or otherwise with which this substitution takes place will depend upon the readiness with which this linking is broken or weakened. It is very difficult to compare the relative facility with which the processes of acetylation and methylation occur, but acetylation of the hydroxyl in the 1-position in the presence of a catalyst takes place so readily that it may be assumed to occur with more facility than the process of methylation. Even if this is so, it is difficult to understand why the acetyl group, which, similarly to the methyl group, favours the 2-position, should wander to the 1-position in the circumstances mentioned above, unless indeed 1-acetylalizarin 2-methyl ether is a more stable substance than 2-acetylalizarin 1-methyl ether.* Experiments to determine whether a conversion of the latter into the former can be effected are in progress, and the behaviour of other acyl groups in similar circumstances is also being studied.

Experimental.

Monoacetylalizarin.—A mixture of commercial alizarin (5 g.), potassium acetate (2·5 g.), and acetic anhydride (25 c.c.) is kept for 24 hours, and then diluted with alcohol. The product, collected after 1 hour and recrystallised repeatedly from alcohol–acetic acid, separates in golden-yellow needles, m. p. 204—206° (Found: $CH_3{\cdot}CO_2H$, 21·0. Calc., 21·3%).

Methylation. Monoacetylalizarin (2 g.) suspended in purified ether (50 c.c.) was mixed with diazomethane from nitrosomethylurethrane (12 c.c.) in ether (200 c.c.). After 5 days, the crystals were collected (1·8 g.) and the mother-liquor was evaporated to dryness; the viscid residue, on digestion with methyl alcohol, deposited a further 0·16 g. of acetylalizarin monomethyl ether (Found: $CH_3{\cdot}CO_2H$, 20·3. $C_{17}H_{12}O_5$ requires $CH_3{\cdot}CO_2H$, 20·2%). After hydrolysis with hydrochloric acid in the presence of acetic acid, the product, which sintered at 170° and melted at 217°, gave, after two or three recrystallisations from alcohol, orange-red needles,

* That the methyl of alizarin 1-methyl ether is loosely held, is evident from the fact that in presence of boiling baryta water, gradual hydrolysis occurs, with formation of barium alizarate.

m. p. 229—230° (Found: C, 70·8; H, 4·05. $C_{15}H_{10}O_4$ requires C, 70·9; H, 3·9%).

The *acetyl* derivative, obtained in yellow needles, melted at 204—206° and there could be no doubt that this, the main product of the reaction, is alizarin 2-monomethyl ether.

The alcoholic filtrate from this substance was evaporated to dryness, the residue dissolved in hot alcohol, and, after the addition of a little ammonia, baryta water was added drop by drop so long as a precipitate, consisting mainly of barium alizarate 2-methyl ether, was formed. This was removed, and on acidifying the bright red filtrate fine, hair-like needles (0·18 g.) separated.* This substance, which became opaque at 100° with loss of water of crystallisation, a characteristic property of alizarin 1-methyl ether, was purified by conversion into the ammonium salt (*loc. cit.*) and recrystallisation from benzene, from which it separated in pale yellow needles, m. p. 179—181° (Found: C, 70·9; H, 4·0. Calc., C, 70·9; H, 3·9%).

Since the acetyl derivative melted at 210—212°, there can be no doubt that this substance was identical with the alizarin 1-methyl ether of Chay root. By fractionally crystallising the diazomethane reaction product of 2-acetylalizarin (2 g.) from a mixture of alcohol and acetic acid, 2-acetylalizarin 1-methyl ether could be isolated in the pure condition (0·3 g. approx.).

Diacetylanthragallol.—A mixture of anthragallol (5 g.), acetic acid (15 c.c.), and acetic anhydride (7 c.c.) was treated in the cold with pyridine (2 c.c.) and kept for about 18 hours. The yellow, crystalline precipitate (5·79 g.) (filtrate A) gave on recrystallisation from acetone 4·3 g. of long, thin plates, m. p. 223—224° (Found: $C_{14}H_8O_5$, 74·4. $C_{18}H_{12}O_7$ requires $C_{14}H_8O_5$, 75·3%).

The filtrate A contained some triacetylanthragallol, which was isolated in a slightly impure condition, m. p. 175—180° (Found: $C_{14}H_8O_5$, 66·9. $C_{20}H_{14}O_8$ requires $C_{14}H_8O_5$, 67·02%).

Methylation. Diacetylanthragallol (2 g.), in ether (50 c.c.) cooled by ice, was treated with diazomethane from nitrosomethylurethrane (8 c.c.) in ether (250 c.c.), and the mixture kept for 2 days. The crystalline suspension (1 g.), after being washed with ether, melted at 145—152°. The filtrate, washed with a little 1% sodium hydroxide solution and partially evaporated, gave 0·75 g. of crystals (filtrate A). By recrystallisation from acetone, large, yellow, prismatic needles were obtained, m. p. 152—154° (Found: C, 64·55; H, 4·15; CH_3, 4·3. $C_{19}H_{14}O_7$ requires C, 64·4; H, 3·95; CH_3, 4·23%).

Hydrolysis with hydrochloric acid in acetic acid solution gave

* In a second experiment 4 g. of monoacetylalizarin gave 0·32 g. of alizarin 1-methyl ether.

78·5% of a yellow, crystalline precipitate which separated from much benzene as a spongy mass of microscopic needles, m. p. 218—220° (Found: C, 66·9; H, 3·7; CH_3, 5·55%).

This substance dissolves in dilute alkali with a scarlet colour and is evidently *anthragallol 2-monomethyl ether*, since the alkali solutions of anthragallol 1- and 3-methyl ethers have a blue or bluish-violet tint. The filtrate A was evaporated to dryness and the residue dissolved in hot alcohol mixed with a few drops of ammonia. On keeping, violet-black crystals of an ammonium salt separated which, on drying at 100°, evolved ammonia, yielding an orange-red mass. By recrystallisation from alcohol, this gave red needles (0·3 g.), m. p. 239—241° (Found: C, 66·6; H, 3·9; CH_3, 5·6. $C_{15}H_{10}O_5$ requires C, 66·7; H, 3·7; CH_3, 5·55%).

It dissolves in dilute alkalis with a deep blue colour and dyes mordanted wool the following alizarin-like shades: *chromium*, violet-maroon; *aluminium*, pale maroon; *tin*, orange-red; *iron*, dead black. The diacetyl derivative, obtained as fine, flat, yellow needles, melted at 203—205° (Found: C, 64·5; H, 4·2. $C_{19}H_{15}O_7$ requires C, 64·4; H, 3·95%).

For reasons given in the introduction, this compound is evidently *anthragallol 1-methyl ether*.

Tetra-acetylquercetin.—A mixture of monopotassium quercetin (10 g.) and acetic anhydride (100 g.) was kept for 2 hours. The semi-solid mass was mixed with alcohol; the crystals were then collected and recrystallised from alcohol–acetic acid until the melting point of the colourless, silky needles was constant at 188—190° (Found: $C_{15}H_{10}O_7$, 64·4. $C_{23}H_{18}O_{11}$ requires $C_{15}H_{10}O_7$, 64·25%).

Methylation. Tetra-acetylquercetin suspended in ether was very little attacked by diazomethane and after keeping for 2 days contained only 1·08% of methyl. Better results were obtained by treating the substance (2 g.), dissolved in tetrachloroethane (10 c.c.), with the diazomethane from nitrosomethylurethane (8 c.c.) in ether (125 c.c.). After 4 days, the crystalline deposit (1·7 g.) was collected, and from the filtrate, by removal of the ether by evaporation and the tetrachloroethane by distilling with steam, a colourless, viscid product was isolated from which, by solution in hot alcohol and keeping, a second crop of crystals was obtained. The product was hydrolysed with hydrochloric acid in the usual manner and the precipitate, which consisted largely of an oxonium salt, was repeatedly washed with water to decompose the latter. The product was then dissolved in much alcohol, the solution concentrated until crystallisation commenced, and the operation repeated. The *quercetin monomethyl ether* separated in prismatic

needles, m. p. 305—308° (Found: C, 60·65; H, 4·2; CH_3, 4·2. $C_{16}H_{12}O_7$ requires C, 60·75; H, 3·8; CH_3, 4·6%).

This methyl ether closely resembles rhamnetin (*loc. cit.*) as regards its sparing solubility in solvents, but, on the other hand, it is almost colourless, whereas rhamnetin is yellow. Dilute alkalis dissolve it with an orange coloration and on hydrolysing its acetyl derivative with mineral acids, orange-red oxonium salts can be obtained which crystallise in needles.

The *tetra-acetyl* derivative crystallises from acetone in minute, colourless needles which sinter at 199° and melt at 202—204° (Found: C, 59·5; H, 4·2. $C_{24}H_{20}O_{11}$ requires C, 59·5; H, 4·1%).

Only by very slow deposition from a mixture of acetic anhydride and alcohol can the acetyl derivative be obtained in fair-sized, prismatic needles, whereas acetylrhamnetin crystallises readily in long needles, m. p. 191—193°. When the acetyl compound was digested with boiling alcoholic potassium acetate, lemon-yellow needles of the *monopotassium* salt were gradually deposited, and these were washed with alcohol (Found: K, 11·1. $C_{16}H_{11}O_7K$ requires K, 11·0%).

This potassium salt dissolves in boiling water to form a pale yellow solution, from which on rapid cooling it separates unchanged. On longer digestion, however, some hydrolysis occurs with deposition of the quercetin methyl ether, though it is more resistant to hydrolysis than monopotassium quercetin itself.

The hydrolysis of the quercetin monomethyl ether was effected by heating with methyl-alcoholic potash at 180° for 3 hours. The product freed from alcohol was dissolved in water, and the solution acidified, filtered, and extracted with ether; the syrupy residue obtained by evaporation was then dissolved in sodium bicarbonate solution, and again extracted with ether. The viscid product thus isolated gave with diazobenzene in presence of sodium carbonate a dull red precipitate, which was dried, extracted with boiling alcohol to remove resin, and then crystallised from alcohol–acetic acid. The glistening, orange-red crystals, m. p. 253—255°,* evidently consisted of benzeneazophloroglucinol monomethyl ether. In a second experiment air was aspirated through a dilute alkaline solution of the quercetin methyl ether and, from the brown liquid, phloroglucinol monomethyl ether could again be isolated in the form of its benzene azo-compound.

For reasons given in the introduction, this quercetin monomethyl ether must contain the methoxy-group in the position 5, adjacent to the carbonyl group (IV). The methylation of this hydroxyl

* The m. p. 250—252° previously given for this compound (*loc. cit.*) is slightly too low.

group has no influence on the tinctorial property of quercetin, as dyeing experiments employing mordanted woollen cloth show: *chromium*, red-brown; *aluminium*, orange-yellow; *tin*, bright orange; *iron*, olive-black.

These shades were identical with those given by a sample of quercetin dyed at the same time (J., 1902, **81**, 473) and as quercetin and rhamnetin dye alike (Perkin and Allison) there can be no doubt that the phloroglucinol hydroxyl groups of quercetin do not affect its tinctorial property.

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CCLVI.—*Hydrogen and Oxygen Electrode Titrations of Some Dibasic Acids and of Dextrose.*

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APART from the recent work of Auerbach and Smolczyk (*Z. physikal. Chem.*, 1924, **110**, 83), the study of the ionisation of dibasic acids has been confined to solutions containing (*a*) the free acids and (*b*) the acid salts only, instead of to solutions which are typical of the whole courses of neutralisation. Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 847) obtained several titration curves with the hydrogen electrode, but as he used fairly concentrated solutions and appears to have aimed at an accuracy in his *E.M.F.* measurements of about a centivolt, his curves are useless for the purpose of calculating dissociation constants.

Auerbach and Smolczyk used the quinhydrone electrode in their titrations and derived formulæ by which the dissociation constants could be calculated from their data. Although their equations are based on the assumption that the salts formed in dilute solutions may be taken as being completely dissociated, they used $N/10$-acid and $N/8$-alkali solutions. The amounts of alkali used in their titrations were very small, being as a rule only 8 c.c. It is remarkable that such fundamental titrations should have been carried out with an electrode other than the hydrogen electrode. Some time before the appearance of Auerbach and Smolczyk's paper, the author had used the hydrogen electrode to titrate solutions of acids which were more dilute and required much larger volumes of alkali. Those titrations had been made for the purpose of comparing them with those given by oxygen electrodes; as the accuracy of the voltages obtained with the hydrogen electrode was of the order of a millivolt, it was considered that the curves would furnish an excellent

method of testing the applicability of the formulæ of Auerbach and Smolczyk.

The titration of dextrose has been included in this communication as it is of importance in connexion with some work to be published later.

Experimental.

Part I. *The Hydrogen Electrode.*

The problem of preparing hydrogen electrodes which are immediately sensitive to changes in hydrogen-ion concentration has been one of some difficulty, and this appears to have been the experience of previous experimenters. Thus Böttger (*Z. physikal. Chem.*, 1897, **24**, 251), who first used the hydrogen electrode for titration work, failed to obtain good results with platinised platinum and resorted to gold electrodes coated with palladium black. Andrews (*J. Biol. Chem.*, 1924, **50**, 479) has, however, found palladium black on platinum to be less trustworthy than platinum black. Treadwell and Weiss (*Helv. Chim. Acta*, 1920, **2**, 433) stated that the ordinary platinum electrode required too much time to come to equilibrium to be of use in titrations, and they also preferred palladinised gold.

For ordinary purposes, there is no doubt that the hydrogen electrode when made of platinised platinum does attain, if given sufficient time, true equilibrium, independent of the depth of the platinum black layer. Platinum foil electrodes having a thick coating of platinum black require, in general, an appreciable time before the true *E.M.F.*'s are attained, and are therefore unserviceable for titrations. The efficient electrodes which have been prepared have invariably been made of highly polished platinum foil covered with thin deposits of platinum black such as may be deposited from the usual platinising solution in 5 minutes, the current being reversed every half-minute and a vigorous evolution of gas maintained. Half a dozen electrodes were prepared at a time from which were chosen two electrodes which gave the same *E.M.F.* within a millivolt throughout the entire titration. These two electrodes were used together and the results were taken as accurate if they showed the same *E.M.F.* immediately the current of hydrogen was stopped. Other efficient electrodes were always kept in readiness in case one suddenly became erratic or sluggish, which was especially apt to occur when the electrode was being subjected to a rapid change in hydrion concentration.

The electrodes were of the Hildebrand pattern (*loc. cit.*) and the titrations were performed in the way described previously (J., 1924, **125**, 1576). The results obtained are given in the first two

columns of Tables I—V, the *P.D.*'s being recorded to the nearest millivolt.

TABLE I.

Titration of 100 c.c. of 0·0255*M*-Oxalic Acid with 0·100*N*-NaOH at 18°.

C.c. of NaOH.	*E.M.F.* against *N*-calomel. —Volt.	p_H.	Conc. of free $H_2C_2O_4$ $\times 10^2$.	a.	$[H_2C_2O_4]$ (undissociated) $\times 10^3$.	$[HC_2O_4']$ $\times 10^2$.	K_1.
0	0·378	1·65	2·55	0·89	2·90	2·26	0·19
2·5	0·382	1·72	2·15	0·90	2·15	2·18	0·19
5·0	0·385	1·75	1·99	0·88	2·49	2·23	0·17
7·5	0·389	1·84	1·67	0·87	2·14	2·15	0·15
10·0	0·393	1·91	1·41	0·88	1·69	2·15	0·16
12·5	0·397	1·98	1·16	0·92	0·92	2·17	0·25
15·0	0·403	2·08	0·91	0·91	0·82	2·13	0·22
17·6	0·409	2·18	0·67	0·98	0·13	2·15	1·32
20·0	0·418	2·34	0·46	1·00	—	—	—
22·0	0·429	2·53	0·29	1·03	—	—	—
23·5	0·437	2·67	0·16	1·32	—	—	—
24·5	0·444	2·79	0·08	2·02	—	—	—
25·1	0·446	2·83	0·03	4·68	—	—	—

			$Na_2C_2O_4$.	$NaHC_2O_4$.	$K_2 \times 10^4$.
26·0	0·453	2·95	0·5	25·0	0·23
27·0	0·457	3·02	1·5	24·0	0·60
28·0	0·460	3·07	2·5	23·0	0·93
30·0	0·474	3·31	4·5	21·0	1·05
32·5	0·484	3·48	7·0	18·5	1·25
35·0	0·493	3·64	9·5	16·0	1·36
37·5	0·502	3·80	12·0	13·5	1·43
40·0	0·511	3·95	14·5	11·0	1·48
42·5	0·524	4·18	17·0	8·5	1·33
45·0	0·537	4·40	19·5	6·0	1·29
47·0	0·547	4·58	21·5	4·0	1·43
49·0	0·568	4·94	23·5	2·0	1·35
50·0	0·593	5·37	24·5	1·0	1·04
50·5	0·622	5·88	25·0	0·5	0·67
51·0	0·745	8·00			
52·0	0·894	10·59			
52·5	0·913	10·91			
55·0	0·942	11·42			
57·0	0·956	11·66			
60·0	0·970	11·91			

The third column of each table gives the p_H calculated by means of the Nernst formula. The figures in the remaining columns of the first four tables were obtained on the assumption that the alkali (up to the first equivalent) reacted only with the hydrions arising from the first stage of ionisation and that thereafter it reacted (to the second equivalent) with those from the second dissociation. This assumption, of course, is only justifiable when K_1 is much greater than K_2, but the figures so obtained do give some idea of the process of neutralisation in the cases where the ratio of K_1 to K_2 is small. The fourth columns relating to the first halves

TABLE II.

Titration of 100 c.c. of 0·0250*M*-Tartaric Acid with 0·100 *N*-NaOH at 18°.

C.c. of NaOH.	*E.M.F.* against *N*-calomel —Volt.	p_H.	Conc. of free tartaric acid $\times 10^3$.	α.	$[H_2T] \times 10^3$.	$[HT'] \times 10^3$.	$K_1 \times 10^3$.
0	0·415	2·29	25·0	0·206	19·9	—	1·34
2·5	0·423	2·43	22·0	0·170	18·3	6·18	1·27
5·0	0·430	2·55	19·0	0·149	16·2	7·60	1·33
7·5	0·437	2·67	16·3	0·132	14·1	9·29	1·41
10·0	0·444	2·79	13·6	0·119	12·0	10·7	1·45
12·5	0·450	2·89	11·1	0·115	9·8	13·4	1·61
15·0	0·457	3·02	8·70	0·111	7·7	14·0	1·75
17·5	0·463	3·12	6·38	0·119	5·6	15·7	2·11
20·0	0·470	3·24	4·17	0·138	3·6	17·2	2·76
21·25	0·473	3·29	3·09	0·164	—	—	—
22·5	0·477	3·36	2·04	0·213	—	—	—
23·75	0·480	3·41	1·01	0·382	—	—	—
25·0	0·4835	3·474	—	—	—	—	—

			Na_2T.	NaHT.	$K_2 \times 10^5$.
27·5	0·490	3·59	2·5	22·5	2·87
30·0	0·496	3·69	5·0	20·0	5·08
32·5	0·506	3·87	7·5	17·5	5·85
35·0	0·514	4·00	10·0	15·0	6·62
37·5	0·523	4·16	12·5	12·5	6·92
40·0	0·529	4·26	15·0	10·0	8·19
42·55	0·540	4·45	17·55	7·45	8·30
45·0	0·551	4·64	20·0	5·0	9·08
46·25	0·559	4·78	21·25	3·75	9·35
47·5	0·571	4·99	22·5	2·5	9·19
48·5	0·587	5·27	23·5	1·5	8·43
49·0	0·604	5·56	24·0	1·0	6·56
49·25	0·616	5·77	24·25	0·75	5·48
49·5	0·637	6·14	24·5	0·5	3·59
49·75	0·664	6·60	24·75	0·25	2·47
50·0	0·822	9·34			
50·5	0·884	10·42			
51·0	0·901	10·71			
52·5	0·928	11·18			
55·0	0·945	11·48			
57·5	0·956	11·66			
60·0	0·961	11·75			

of the titrations therefore contain the concentration of acid minus that which was supposed to be converted into the acid salt. The degree of dissociation, α, of the free acid given in the fifth column, was obtained by dividing the hydrogen-ion concentration by the concentration of the acid. Column 6 gives the concentration of undissociated acid. The concentrations of HR′ ions given in the next column represent the sum of the concentrations of NaHR (taken as completely dissociated into $Na^{\cdot}$ and HR′) and the HR′ ions from the free H_2R. In the last column the values of K_1 ($=[H^{\cdot}][HR']/[H_2R]$ are given.

If the first equivalent of alkali be regarded as producing acid

TABLE III.

Titration of 100 c.c. of 0·0240*M*-Succinic Acid with 0·100*N*-NaOH at 18°.

C.c. of NaOH.	*E.M.F.* against *N*-calomel. —Volt.	p_H.	Conc. of free succinic acid $\times 10^3$.	a.	$[H_2Suc.]$ $\times 10^3$.	$[HSuc.']$ $\times 10^3$.	K_1 $\times 10^5$
0	0·446	2·83	24·0	0·0623	22·5	—	9·95
2·5	0·467	3·19	21·0	0·0309	20·3	3·09	9·86
5·1	0·482	3·45	18·0	0·0198	17·6	5·21	10·51
7·5	0·495	3·67	15·4	0·0140	15·1	7·35	10·28
10·0	0·508	3·90	12·7	0·0099	12·6	9·22	9·23
12·5	0·518	4·07	10·2	0·0083	10·1	11·20	9·36
15·0	0·524	4·18	7·83	0·0085	7·8	13·1	11·3
17·5	0·532	4·32	5·53	0·0088	5·5	14·9	13·2
20·0	0·540	4·45	3·33	0·0106	3·3	16·7	17·8
22·0	0·547	4·58	1·64	0·0162	1·6	18·1	29·8
23·0	0·550	4·63	0·81	0·0290	7·9	18·7	55·9
24·0	0·556	4·73	—	—	—	—	—

			$Na_2Suc.$	$NaHSuc.$	$K_2 \times 10^6$.
25·0	0·557	4·75	1·0	23·0	0·78
27·5	0·564	4·87	3·5	20·5	2·30
30·0	0·570	4·97	6·0	18·0	3·54
32·5	0·579	5·13	8·5	15·5	4·06
35·0	0·588	5·29	11·0	13·0	4·39
37·5	0·596	5·42	13·5	10·5	4·84
40·0	0·608	5·63	16·0	8·0	4·67
42·5	0·621	5·86	18·5	5·5	4·68
44·0	0·630	6·01	20·0	4·0	4·85
45·0	0·639	6·17	21·0	3·0	4·74
46·1	0·654	6·43	22·1	1·9	4·32
47·0	0·670	6·71	23·0	1·0	4·52
47·25	0·681	6·90	23·25	0·75	3·92
47·5	0·694	7·12	23·5	0·5	3·55
47·75	0·733	7·80	23·75	0·25	1·51
48·0	0·807	9·08			
48·5	0·857	9·95			
49·0	0·885	10·43			
50·0	0·920	11·04			
52·5	0·943	11·44			
55·1	0·956	11·66			
57·5	0·963	11·79			
60·0	0·969	11·89			

salt only, the addition of further alkali will convert equivalent amounts into Na_2R. Then $K_2 = [H^\cdot][R'']/[HR']$ may be calculated if the NaHR and Na_2R be taken as either completely or equally dissociated into $Na^\cdot$ and HR′, and $2Na^\cdot$ and R″ respectively, in which case $K_2 = [H^\cdot](x - y/2)/(y - x)$, where x is the number of c.c. of NaOH added, and y the number of c.c. required for neutralisation. For the second half of the titrations, the fourth and fifth columns give the number of c.c of alkali, $(y - x)$ and $(x - y/2)$ respectively, which are proportional to the respective concentrations of NaHR and Na_2R. The values of K_2 thus found are given in the last column.

TABLE IV.

Titration of 100 c.c. of 0·0230*M*-Malonic Acid with 0·100*N*-NaOH at 18°.

C.c. of NaOH.	*E.M.F.* against *N*-calomel. −Volt.	p_H.	Conc. of free malonic acid × 10^3.	α.	$[H_2M]$ × 10^3.	$[HM']$ × 10^3.	K_1 × 10^3.
0	0·411	2·28	23·0	0·263	16·9	—	2·16
2·5	0·420	2·37	20·0	0·211	15·8	6·67	1·79
5·0	0·427	2·50	17·1	0·186	14·0	7·95	1·82
7·5	0·433	2·60	14·4	0·175	11·9	9·65	2·04
10·0	0·440	2·72	11·8	0·161	9·91	11·0	2·12
12·5	0·448	2·86	9·34	0·148	7·95	12·5	2·17
15·0	0·458	3·03	6·96	0·133	6·03	14·0	2·15
17·5	0·470	3·24	4·68	0·123	4·11	15·5	2·16
18·5	0·477	3·36	3·80	0·115	3·36	16·0	2·07
20·0	0·487	3·54	2·50	0·117	2·21	17·0	2·24
21·0	0·495	3·67	1·66	0·128	1·45	17·6	2·58
22·0	0·509	3·85	0·82	0·173	0·68	18·2	3·81
22·5	0·515	4·02	0·41	0·233	0·41	18·5	5·62
23·0	0·520	4·11	—	—	—	—	—

			Na_2M.	NaHM.	K_2 × 10^6.
23·5	0·525	4·19	0·5	22·5	1·42
24·0	0·530	4·28	1·0	22·0	2·38
25·0	0·538	4·42	2·0	21·0	3·63
27·5	0·560	4·80	4·5	18·5	3·86
30·1	0·571	4·99	7·1	15·9	4·56
32·5	0·580	5·15	9·5	13·5	5·02
35·0	0·589	5·30	12·0	11·0	5·43
37·5	0·598	5·46	14·5	8·5	5·93
40·0	0·616	5·77	17·0	6·0	4·80
42·0	0·630	6·01	19·0	4·0	4·61
43·0	0·638	6·15	20·0	3·0	4·70
44·0	0·649	6·34	21·0	2·0	4·76
45·0	0·673	6·76	22·0	1·0	3·83
45·25	0·684	6·95	22·25	0·75	3·34
45·5	0·700	7·23	22·5	0·5	2·67
45·75	0·749	8·08	22·75	0·25	0·76
46·0	0·821	9·32			
46·25	0·849	9·81			
46·5	0·869	10·16			
47·0	0·895	10·60			
48·5	0·925	11·13			
50·0	0·940	11·39			
52·5	0·953	11·61			
55·0	0·961	11·75			
57·5	0·966	11·84			
60·0	0·971	11·92			

The titration curves together with that of dextrose are given in Fig. 1. The curve of the latter shows that dextrose had the effect of depressing the alkalinity of the added sodium hydroxide. The monobasic acid nature of dextrose, $C_6H_{12}O_6 \rightleftharpoons H^{\cdot} + C_6H_{11}O_6'$, is revealed in the formation of salts with the alkali metals. The dissociation constant, $K = [H^{\cdot}][C_6H_{11}O_6']/[C_6H_{12}O_6]$, has been calculated from the various observations made during the titration.

TABLE V.

Titration of 140 c.c. of 0·3572*M*-Dextrose with 0·100*N*-NaOH at 18°.

C.c. of NaOH.	*E.M.F.* against *N*-calomel. —Volt.	p_H.	Conc. of NaOH × 10^3.	Total conc. of NaOH and NaGluc. × 10^3.	Conc. of NaGluc. × 10^3.	Conc. of undiss. glucose.	K = [H·][Gluc′] / [HGluc.] × 10^{13}.
0	0·645	6·27	—	—	—	0·3572	8·07*
0·5	0·808	9·10	0·009	0·356	0·347	0·3557	7·75*
1·0	0·833	9·53	0·025	0·709	0·684	0·3539	5·70
3·0	0·860	10·00	0·07	2·10	2·03	0·3477	5·84
5·0	0·870	10·35	0·16	3·45	3·29	0·3416	4·30
10·0	0·887	10·47	0·21	6·67	6·46	0·3300	6·63
20·0	0·909	10·85	0·51	12·5	12·0	0·3005	5·65
30·0	0·920	11·04	0·79	17·6	16·8	0·2773	5·53
40·0	0·927	11·16	1·05	22·2	21·1	0·2567	5·69
50·0	0·933	11·27	1·35	26·3	24·9	0·2383	5·61
60·0	0·938	11·35	1·62	30·0	28·4	0·2216	5·72
70·0	0·941	11·40	1·82	33·3	31·5	0·2066	6·07
80·0	0·946	11·49	2·24	36·4	34·2	0·1931	5·73
90·0	0·948	11·53	2·46	39·1	36·6	0·1808	5·97
100·0	0·950	11·55	2·57	41·7	39·1	0·1693	6·51

Mean 5·77 × 10^{-13}

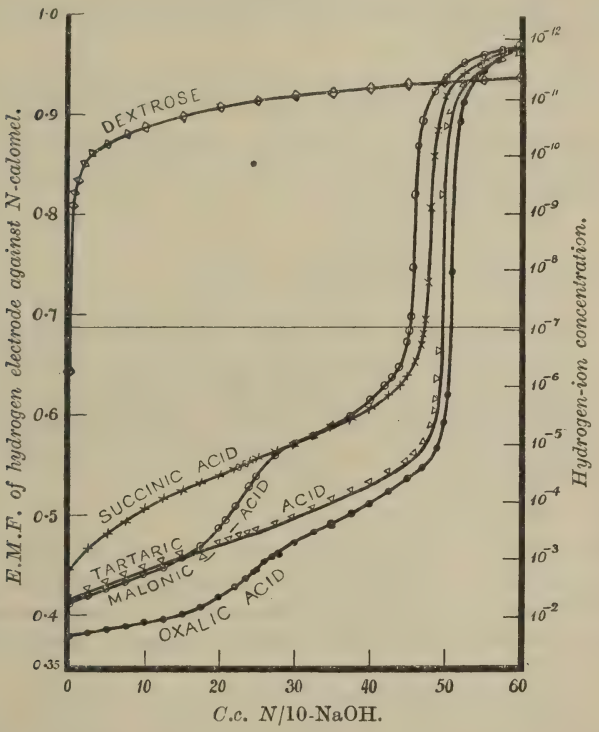
* Omitted in calculating mean.

As the solution remained appreciably alkaline throughout the titration, it was evident that some of the sodium hydroxide had remained uncombined, the concentrations of which were found from the hydrion data, and were equal to $K_w/[H^\cdot]$, K_w at 18° being $10^{-14\cdot14}$, if the dissociation of the alkali be assumed complete.

These concentrations are given in the fourth column, and as the combined concentrations of the sodium hydroxide and the sodium salt of dextrose were equal to the sodium concentrations produced by the added alkali, given in the fifth column, the actual concentrations of sodium glucoside were known (column 6). Then, as the concentrations of sodium glucoside were very small, it followed that these concentrations were very nearly those of the glucoside ion. Thus by knowing the concentrations of undissociated glucose, which in the circumstances were equal to those of unattacked glucose, the affinity constant was found. It will be seen that, except in the first two values, which can only be regarded as approximate in view of the rapid change in hydrion concentration which was then taking place, the values are in fairly good agreement, the average being 5·77 × 10^{-13}. The acid nature of glucose has been previously studied by Cohen (*Proc. K. Akad. Wetensch. Amsterdam*, 1900, **2**, 628) and by Madsen (*Z. physikal. Chem.*, 1901, **36**, 290), both of whom measured the rate of saponification of ethyl acetate by alkaline solutions of dextrose. From the data obtained by the former worker, Osaka (*Z. physikal. Chem.*, 1900, **35**, 673) showed that,

if dextrose be regarded as a monobasic acid, $K = 5{\cdot}9 \times 10^{-13}$, and Euler (*Ber.*, 1906, **39**, 344), using the latter's observations, obtained a value $K = 3{\cdot}6 \times 10^{-13}$ at 18°. Later, Michaelis and Rona (*Biochem. Z.*, 1913, **49**, 248), measuring the p_H values of some alkali–dextrose solutions with the hydrogen electrode, found $K = 6{\cdot}6 \times 10^{-13}$.

FIG. 1.



Calculation of the Dissociation Constants of Dibasic Acids from Titration Curves.

The following equations are based on the mass law and apply to solutions which are so dilute that the sodium salts may be taken as completely dissociated. The equations, however, differ from those of Auerbach and Smolczyk (*loc. cit.*) in that no approximations have been introduced.

Let c = the total concentration of acid, a = total concentration of added alkali, and h = hydrogen-ion concentration. A dibasic acid, H_2R, dissociates thus :

(i) $H_2R \rightleftharpoons H^{\cdot} + HR'$ (ii) $HR' \rightleftharpoons H^{\cdot} + R''$,

such that $K_1 = h[HR']/[H_2R]$ and $K_2 = h[R'']/[HR']$. Then $[H_2R] + [HR'] + [R''] = c$ and $[HR'] + 2[R''] = a - h$. By eliminating the unknowns from these four equations, it is found that

$$K_1 = h^2(a + h)/\{K_2(2c - a - h) - (ah + h^2 - hc)\} \quad \ldots\ldots\ldots (1)$$

$$K_2 = \{h^2(a + h) + K_1(ah + h^2 - hc)\}/K_1(2c - a - h) \quad \ldots\ldots (2)$$

Putting $a_n h_n + h_n^2 - h_n c_n = A_n$, $2c_n - a_n - h_n = B_n$, and $h_n^2\,(a_n + h_n) = D_n$,

then

$$K_1 = D_n/(K_2B_n - A_n) \text{ and } K_2 = (D_n + K_1A_n)/K_1B_n.$$

Hence, by taking any two points on the titration curve whose parameters are respectively A_1, B_1, D_1, and A_2, B_2, D_2, the values of K_1 and K_2 can be found.

Thus

$$K_1 = (B_1D_2 - B_2D_1)/(A_1B_2 - A_2B_1) \quad \ldots\ldots\ldots (3)$$

$$K_2 = (A_1D_2 - A_2D_1)/(B_1D_2 - B_2D_1) \quad \ldots\ldots\ldots (4)$$

Many of the values of K_2 for dibasic acids have hitherto been obtained from determinations of the hydrogen-ion concentrations of solutions of the acid salts and calculated by means of a formula, worked out by Noyes (*Z. physikal. Chem.*, 1893, **11**, 495), identical with (2), for when $a = c$, as is the case with an acid salt, NaHR, the equation becomes

$$K_2 = h^2(c + K_1 + h)/K_1(c - h) \quad \ldots\ldots\ldots (5)$$

A disadvantage of using the acid salt only is that the dissociation of the acid to the second stage in such a solution is often very small and consequently necessitates an accuracy in the measurements of the hydrion concentration which is rarely obtained. Another drawback is that the formula involves K_1.

Auerbach and Smolczyk used the supposed identity $K_1K_2 = h^2_{x_{a_1/2}}$ as a criterion of the accuracy of the values of K_1 and K_2 calculated from their formulæ. It seems hardly necessary to state that the hydrogen-ion concentrations of dilute solutions of acid salts, or of solutions undergoing titration when half the total amount of alkali has been added, are functions of the concentrations of the salts. The measurements of Drucker (*Z. physikal. Chem.*, 1921, **96**, 419) show that at 20° the p_H of solutions of potassium hydrogen tartrate varies from 3·47 in 0·025M-solution to 3·55 in 0·01M-solution and to 3·93 in 0·001M-solution. Such variations render the above relationship useless, especially when applied to Auerbach and Smolczyk's titrations in which the concentration of acid salt was 0·036M-$NaHC_4H_4O_6$ at the mid-point of the tartaric acid titration. It follows also from equation (5) that K_1K_2 can be equal to h^2 only

when the expression $(c + K_1 + h)/(c - h)$ is equal to unity, *i. e.*, when $K_1 = -2h$. This condition can never be obtained, and, as the data given in this paper show, the expression rarely even approximates to 1, except where K_1 is negligibly small compared with c, as in the case of succinic acid.*

TABLE VI.

Calculation of the Dissociation Constants of Oxalic Acid.

C.c. of NaOH.	K_1. Form. 3.	K_1. Table I.	$K_2 \times 10^4$. Form. 4.	$K_2 \times 10^4$. Table I.	C.c. of NaOH.	K_1. Form. 3.	K_1. Table I.	$K_2 \times 10^4$. Form. 4.	$K_2 \times 10^4$. Table I.
5·0 / 45·0	0·20	0·17	1·31	1·29	0 / 30·0	0·17	0·19	1·26	1·05
10·0 / 40·0	0·14	0·16	1·52	1·48	0 / 40·0	0·17	0·19	1·52	1·48
15·0 / 35·0	0·15	0·22	1·45	1·36	0 / 45·0	0·18	0·19	1·31	1·29
20·0 / 30·0	0·16	—	1·26	1·05	Mean	0·17	0·18	1·34	1·38
0 / 25·5	0·17	0·19	1·05	—					

TABLE VII.

Dissociation Constants of Tartaric Acid.

C.c. of NaOH.	$K_1 \times 10^3$. Form. 3.	A. & S.	Table II.	$K_2 \times 10^5$. Form. 4.	A. & S.	Table II.
5 / 45	1·22	0·66	1·33	9·56	9·77	9·08
10 / 40	1·24	1·23	1·45	9·30	7·25	8·19
15 / 35	1·30	1·10	1·75	8·56	9·03	6·62
20 / 30	1·22	1·08	2·76	10·61	10·84	5·08
0 / 25	1·28	—	1·34	9·68	—	—
5 / 30	1·21	0·63	1·33	10·65	14·87	5·08
0 / 15	1·29	—	1·34 / 1·75	9·16	—	—
20 / 30	1·29	—	—	9·64	—	—
0 / 5	1·35	—	1·33 / 1·27	[−1·24]	—	—
40 / 50	[0·91]	—	—	9·65	—	8·19 / 9·08
Mean	1·27	0·94	—	9·65	10·35	—

* The author's attention has been directed to the following. If the supposed identity, $K_1K_2 = h^2$, be substituted in Noyes's equation, it follows that K_1 must be equal to $4K_2$. As a rule, K_1 is greater than $4K_2$, but it will be observed from the following tables that in the cases of succinic and tartaric acids, where the ratio $K_1 : K_2$ is not considerable, the product K_1K_2 is only a little greater than h^2.

TABLE VIII.

Dissociation Constants of Succinic Acid.

C.c. of NaOH.	$K_1 \times 10^5$. Form. 3.	A. & S.	Table III.	$K_2 \times 10^6$. Form. 4.	A. & S.	Table III.
5 } 45 }	10·20	9·31	10·51	5·40	4·82	4·74
10 } 40 }	8·33	8·14	9·23	5·00	5·00	4·67
15 } 35 }	8·70	8·61	11·29	5·23	5·23	4·39
20 } 30 }	8·20	10·10	17·84	5·85	5·84	3·54
0 } 24 }	9·90	—	9·95	3·50	—	—
0 } 15 }	9·91	—	{ 9·95 { 11·29	[2·44]	—	—
25 } 35 }	[7·65]	—	—	5·32	—	4·39
Mean	9·21	9·04	—	5·30	5·22	—

TABLE IX.

Dissociation Constants of Malonic Acid.

C.c. of NaOH.	$K_1 \times 10^3$. Form. 3.	A. & S.	Table IV.	$K_2 \times 10^6$. Form. 4.	A. & S.	Table IV.
0 } 45 }	1·96	—	2·16	3·83	—	3·83
5 } 40 }	1·81	0·89	1·82	4·82	4·80	4·80
10 } 35 }	2·10	1·45	2·12	5·46	5·49	5·43
15·0 } 30·1 }	2·10	1·70	2·15	4·67	4·67	4·56
20 } 25 }	1·99	1·81	2·24	4·51	4·70	3·63
0 } 23 }	2·16	—	2·16	3·19	—	—
Mean	2·02	1·46	2·11	4·41	4·92	4·45

Table VI gives the values of the dissociation constants of oxalic acid calculated from the data of pairs of typical points on the titration curve from equations (3) and (4). The values recorded in Table I for the appropriate stages of the titration are also given for comparison. Auerbach and Smolczyk did not use their formula for oxalic acid, as they considered it to be too strong an acid. In Tables VII, VIII, and IX, the values of K_1 and K_2 are given for tartaric, succinic, and malonic acids respectively, as calculated from formulæ (3) and (4), also from those of Auerbach and Smolczyk, together with the comparable values already given in Tables II to IV.

Discussion.

It will be seen from Tables I and VI that the first stage of dissociation of oxalic acid is that of a strong acid and consequently does not rigidly obey the mass law. Chandler (*J. Amer. Chem. Soc.*, 1908, **30**, 705), however, found by the conductivity method that K_1 at 25° was equal to $3{\cdot}8 \times 10^{-2}$, and Drucker (*Z. physikal. Chem.*, 1920, **96**, 381) obtained a mean value $5{\cdot}7 \times 10^{-2}$ at 18°, the actual values varying from 5·2 to $8{\cdot}3 \times 10^{-2}$. The values of K_1 given in Table IV are much higher than these and, as Table I shows, correspond to a degree of dissociation of 0·89. For the value of K_1 to have been that obtained by Drucker, the *P.D.* for the free acid should have been 4 millivolts greater. The *E.M.F.* here recorded has, however, been obtained repeatedly. The values of K_1 given in Tables I and VI are fairly concordant over the first part of the titration, but, as Table I shows, α began to increase after 10 c.c of alkali had been added, due to the appearance of hydrions from the second stage of ionisation. The values of K_1, 0·15 and 0·16, calculated by means of equation (3) from the respective pairs of points, 15, 35 and 20, 30, show that a part only of the change in hydrion concentration thereafter was due to dissociation in the first stage.

The values of K_2 for oxalic acid calculated by the two methods at the different stages of the titration are in good agreement, although the value $1{\cdot}05 \times 10^{-4}$ obtained at 30 c.c. (Table I) is somewhat low. The value of K_2 obtained from the points 0 and 25·5 is also low, and it is at this point that equation (4) becomes, in effect, the well-known Noyes equation. The values of K_2 found in the later stages of the titration show a tendency to increase, which is no doubt largely due to the neglected ionisation of the acid and normal salts formed. The first four low values of K_2 given in Table I for the first part of the second half of the titration appear to be due to the fact that all the ions arising from the first stage of dissociation had not been neutralised. The last two values of K_2 in Table I are merely approximate, for, as the curve shows, they refer to a stage in the titration during which an exceedingly rapid change in hydrogen-ion concentration was taking place. From the values of the constants K_1 and K_2 given in Tables I and VI it will be seen that at the beginning of the titration the first dissociation only came into play, in the middle portion, represented in the diagram by the inflexion, both stages of dissociation were affected, and in the last third of the titration the second stage of dissociation alone functioned.

The average value of K_1 for oxalic acid is 0·17 and of K_2, $1{\cdot}34 \times 10^{-4}$, and therefore $K_1 = 1269\ K_2$. Chandler obtained values of K_1 ranging from $840K_2$ to $1087\ K_2$; and Drucker's values of K_2

ranged from 1·5 to 9 × 10^{-5}, the average value being 6·9 × 10^{-5}, and thus $K_1 = 825K_2$, the actual values ranging from $3800K_2$ to $650K_2$. The value now found for K_2 is thus somewhat higher than the value obtained hitherto, but it does account for the changes in hydrion concentration which take place during the process of neutralisation within narrow limits. The great difference in the two dissociation constants explains why they may be calculated in the manner adopted in Table I from the data given in the first and the last stage of the titration.

The data given in Table VII for the dissociation constants of tartaric acid calculated from formulæ (3) and (4), and from those of Auerbach and Smolczyk, show that more consistent values are obtainable from the former equations. Several values have been calculated by means of the equations given in this paper for which no corresponding values from Auerbach and Smolczyk's formulæ have been given, their formulæ having been designed for pairs of points, one on each side of the mid-point. The values of K_1 give a mean of 1·27 × 10^{-3} when calculated from equation (3) and 0·94 × 10^{-3} by Auerbach and Smolczyk's formula, and $K_2 =$ 9·65 × 10^{-5} and 10·35 × 10^{-5} by the respective methods. Taking K_1 and K_2 as 1·27 × 10^{-3} and 9·65 × 10^{-5} respectively, $K_1 = 13K_2$, and thus it becomes clear why the points 0 and 15 could be employed to calculate the value of K_2, as an appreciable quantity of the normal salt must have then been formed. The last two sets of data show that the extent to which the change in p_H between the points 0 and 5 was governed by K_2, and between the points 40 and 45 by K_1, was so small that satisfactory values of the respective constants could not be calculated.

Auerbach and Smolczyk found from their curve, $K_1 = 8{\cdot}96 \times 10^{-4}$ and $K_2 = 7{\cdot}46 \times 10^{-5}$ at 20°, and therefore $K_1 = 12K_2$. Other workers have found for K_1, 9·7 × 10^{-4} at 25° (Ostwald, *Z. physikal. Chem.*, 1889, **3**, 369; Walden, *ibid.*, 1891, **8**, 483) and 1·17 × 10^{-3} (Drucker, *ibid.*, 1920, **96**, 382), and the values of K_2 range from 2·9 to 6·9 × 10^{-5} (Smith, *ibid.*, 1898, **25**, 260; Wegscheider, *Monatsh.*, 1902, **23**, 635; McCoy, *J. Amer. Chem. Soc.*, 1908, **30**, 694; Datta and Dhar, J., 1915, **107**, 824; Paul, *Z. Elektrochem.*, 1915, **21**, 552; 1917, **23**, 70; *Z. physikal. Chem.*, 1924, **110**, 417; Drucker, *loc. cit.*; Larsson, *Z. anorg. Chem.*, 1922, **125**, 281). The values of K_1 given in Table II are approximately true for the first three readings, and the highest values of K_2 are a little lower than the actual value.

There seems to be little difference between the respective values of K_1 and K_2 for succinic acid (Table VIII) as calculated by the two methods. The values based on the assumptions made in Table III

for the first part of the titration, even in the initial stages, appear to be somewhat too high, and those for the main portion of the second stage of the titration to be a little too low. The values obtained for the middle part of the titration are erratic. Excluding the values of K_1 and K_2 given in brackets in Table VII, which were obtained from pairs of points each lying in the extreme halves of the curves, $K_1 = 9{\cdot}21 \times 10^{-5}$ and $K_2 = 5{\cdot}30 \times 10^{-6}$ and therefore $K_1 = 17K_2$; and it happens that the mean values given by Auerbach and Smolczyk's formulæ give the same relationship. Auerbach and Smolczyk obtained from their titration data at 20° $K_1 = 6{\cdot}86 \times 10^{-5}$ and $K_2 = 3{\cdot}97 \times 10^{-6}$, whereas previous workers have found $K_1 = 6{\cdot}55 \times 10^{-5}$ at 25° (Ostwald, *Z. physikal. Chem.*, 1889, **3**, 272; White and Jones, *Amer. Chem. J.*, 1910, **44**, 197) and values for K_2 ranging from 2·2 to 4·3 $\times 10^{-6}$ (Noyes, *Z. physikal. Chem.*, 1893, **11**, 495; Smith, *loc. cit.*; Datta and Dhar, *loc. cit.*; Chandler, *loc. cit.*; Larsson, *loc. cit.*). The data of Chandler show a variation in the ratio of K_1 to K_2 from 15·5 to 26·6.

Contrary to the good agreement between the values for K_1 for succinic acid obtained by the two methods of calculation, Table IX, referring to malonic acid, shows that whereas concordant values are given by equation (3) and Table IV, the values calculated from Auerbach and Smolczyk's formula are low and increase as the points from which they were calculated approach the mid-point of the curve. The values of K_2, however, found by each of the three methods are in good agreement. Taking $K_1 = 2{\cdot}02 \times 10^{-3}$ and $K_2 = 4{\cdot}41 \times 10^{-6}$, it follows that $K_1 = 476K_2$, as compared with Chandler's results at 25°, which show a variation of K_1 from $357K_2$ to 493 K_2 when the latter constant was determined by McCoy's partition method, whereas K_1 is given as $1{\cdot}58 \times 10^{-3}$, which was also obtained by Ostwald (*loc. cit.*), and K_2 as $2{\cdot}1 \times 10^{-6}$, from conductivities, and thus $K_1 = 752K_2$. Other values are: K_1, $1{\cdot}61 \times 10^{-3}$ at 25° (White and Jones, *loc. cit.*) and K_2, $1{\cdot}41 \times 10^{-6}$ at 25° (Datta and Dhar, *loc. cit.*).

It was mentioned on p. 1904 that Auerbach and Smolczyk used the expression $K_1K_2 = h^2$, where h was the hydrogen-ion concentration at the point of half neutralisation, and this could only be true if $(c + K_1 + h)/(c - h)$ in the expression $K_2 = h^2 (c + K_1 + h)/K_1(c - h)$ was equal to unity. Putting $\lambda = (c + K_1 + h)/(c - h)$, then $K_1K_2 = \lambda h_2$.

Table X gives the values of λ as calculated from (*a*) the data obtained at the mid-points of the titrations, the mean values of K_1 obtained from formula (3) being used, (*b*) the products K_1K_2 divided by h^2, the constants having been calculated from equations (3) and (4), λ_B, and (*c*) the products K_1K_2 divided by h^2, the constants used

being those found by Auerbach and Smolczyk's formulæ, λ_A. The numbers given in brackets show the variations in the products and the corresponding changes produced in the values of λ.

TABLE X.

			Form. 3 and 4.		A. & S.'s form.	
Acid.	h^2.	λ.	K_1K_2.	λ_B.	K_1K_2.	λ_A.
Oxalic	$1{\cdot}76\times10^{-6}$	10·1	$2{\cdot}28\times10^{-5}$	13·0	—	—
			(1·83—2·52)	(10·4—14·3)		
Tartaric	$1{\cdot}13\times10^{-7}$	1·10	$1{\cdot}23\times10^{-7}$	1·09	$0{\cdot}97\times10^{-7}$	0·86
			(1·11—1·29)	(0·98—1·14)	(0·64—1·17)	(0·57—1·04)
Succinic	$3{\cdot}44\times10^{-10}$	1·01	$4{\cdot}88\times10^{-10}$	1·42	$4{\cdot}72\times10^{-10}$	1·37
			(3·46—5·50)	(1·01—1·60)	(4·07—5·91)	(1·18—1·72)
Malonic	$6{\cdot}11\times10^{-9}$	1·12	$8{\cdot}90\times10^{-9}$	1·45	$7{\cdot}18\times10^{-9}$	1·17
			(6·89—11·46)	(1·13—1·87)	(4·27—8·51)	(0·70—1·39)

It is evident from the table that only in the case of succinic acid does $\lambda = 1$; the expression $(c + K_1 + h)/(c + h)$ shows that this can be so only when K_1 is exceedingly small and h has become correspondingly small, such as happens to be the case with succinic acid. For the other acids, both K_1 and h are sufficiently large compared with c to render λ appreciably greater than 1, the extreme case being that of oxalic acid, for which $\lambda = 10$. The values of λ_B, whilst being of the same order as λ, show some variations which are due largely to the neglect of the ionisation of the salts formed during the titrations. The values of λ_A show similar, although somewhat greater variations, and these are caused by errors due both to dissociation and to the fact that the Auerbach–Smolczyk formulæ do not yield satisfactory results for K_1 when it happens to be fairly large, *e. g.*, of the order of 10^{-3}.

By an approximate mathematical analysis Auerbach and Smolczyk have shown how the character of the titration curves is determined by the ratio of their dissociation constants. Thus when K_1 is greater than $16K_2$ the curve will have an inflexion in the middle, whereas when $K_1 = 16K_2$ the curve will be a straight line, and when K_1 is less than $16K_2$ the curve will be similar to that of a monobasic acid. The curves of oxalic and malonic acids, the second dissociation constants of which are considerably less than $1/16K_1$, *viz.*, 1/1269 and 1/476 respectively, have each large inflexions (Fig. 1), whereas in that of succinic acid an exceedingly small inflexion is perhaps just discernible, and the curve for tartaric acid ($K_1 = 13K_2$) is straighter.

It is striking that the first two members—oxalic acid and malonic acid—of the saturated dibasic acid series,

$$HO_2C{\cdot}[CH_2]_n{\cdot}CO_2H,$$

should exhibit such a great difference in their two dissociation

constants, in each case the first constant being several hundred times the second, as compared with the next member, succinic acid, the first constant of which is only seventeen times the second. The dissociation constants found by Chandler (*J. Amer. Chem. Soc.*, 1908, **30**, 713) for the remaining members of the series up to sebacic acid, $n = 8$, reveal the remarkable fact that the values of K_2 from malonic acid upwards are all approximately equal and of the order 10^{-6}, and that there is only a small diminution in K_1 of the ascending acids of the series, but they are all of the order given by succinic acid, *viz.*, 10^{-5}. Hence the titration curves of these acids will be similar to that of succinic acid and, in fact, almost coincident with it.

The views relating to the acidity of dibasic acids held at the present time appear to be those which were first enunciated by Ostwald (*Z. physikal. Chem.*, 1892, **9**, 553) and are based on the electrostatic charges carried by the various ions and the influence that may be exerted by virtue of the proximity of the carboxyl groups. He considered that in the ionisation of a dicarboxylic acid the negative charge carried by the anion, arising from the first dissociation, exerted a force of repulsion on the negative charge carried by the other carboxyl group and that the nearer one carboxyl group was to the other the greater would be this repulsive force, which would therefore tend to prevent the ionisation proceeding to the second stage.

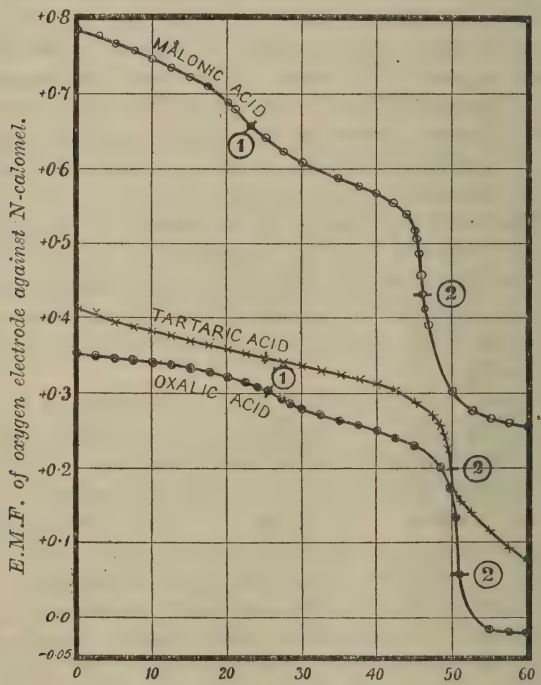
The examples which Ostwald gave were those of fumaric and maleic acids and thus the hypothesis gave excellent support to the van 't Hoff theory accounting for their structure. The hypothesis does not, however, obtain such a marked success when applied to the series in question. It does seem to hold when applied to the first two acids—oxalic and malonic—but it is difficult to see why the interposition of a further methylene group in the case of succinic acid should have such a considerable effect in making K_1 approach K_2 in magnitude. It would have been expected, moreover, that as the chain of methylene groups became longer and longer and the repulsive force between the negative charges held by the carboxyl groups grew less and less, the second stage of dissociation would have become greater and greater, gradually becoming equal to the very slowly decreasing K_1, instead of remaining unchanged.

Part II. *Oxygen Electrode Titrations.*

For the purpose of examining more closely the behaviour of the oxygen electrodes during titrations, three of the acid solutions titrated with the hydrogen electrode were chosen, for their titrations involved changes in hydrogen-ion concentrations which extended over the whole acid zone. 100 C.c. each of 0·0230*M*-malonic acid,

0·0250*M*-tartaric acid, and 0·0255*M*-oxalic acid were titrated at 18° with *N*/10-sodium hydroxide, the oxygen electrode being used in the way outlined in an earlier paper (Britton, J., 1924, **125**, 1572). Observations were made similar to those in the titrations of chromic acid (*loc. cit.*) regarding the initial *E.M.F.*'s, which were again independent of the nature of the acid, and to some extent independent of the initial hydrogen-ion concentration of the solution. As a rule, no two oxygen electrodes ever gave the same *E.M.F.*'s

FIG. 2.



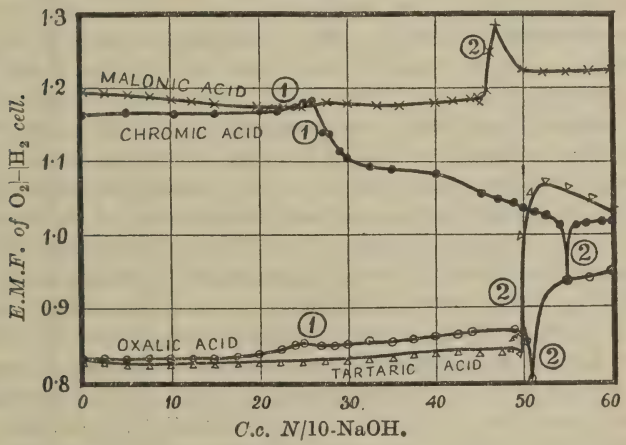
when immersed in the same solution. Typical titration curves are given in Fig. 2, the ordinates being the observed *P.D.*'s between the oxygen electrode and the normal calomel electrode, and the abscissæ the amount of alkali added. The three titrations were made on successive days with the same electrode, of the Hildebrand type but having a platinised platinum wire instead of foil, and were carried out in the order malonic, tartaric, and finally oxalic acid. As the electrode became more and more aged, the *E.M.F.* readings became less positive. The electrodes also tended to become more

and more erratic after having been subjected to rapid changes in hydrion concentration.

Comparison of Oxygen and Hydrogen Electrode Curves.

In the previous paper it was pointed out that, if the oxygen electrode behaved ideally, the algebraic differences between the *E.M.F.*'s given by the oxygen electrode and by the hydrogen electrode at comparable stages of a titration should remain constant, these differences being the *P.D.*'s of the oxygen–hydrogen cell in the various solutions. These differences have been ascertained for each of the three titrations and are plotted in Fig. 3.

Fig. 3.



The *E.M.F.*'s of the oxygen–hydrogen cell extrapolated from the titration curves of the three organic acids show that in the case of malonic acid there was a gradual but small diminution until the first equivalent had been neutralised, after which the *P.D.* remained constant until the end-point had been reached; it then suddenly increased, but afterwards fell to a value somewhat higher than the initial *E.M.F.* The oxalic and tartaric acid titrations, which were performed with electrodes which had become a little aged, produced small and gradual increases in *P.D.* apart from the slight inflexion which occurred at the mid-point of the oxalic acid curve due to a lag in the *E.M.F.* of the oxygen electrode, until the neutralisation was complete; the *E.M.F.* of the oxygen–hydrogen cell then suddenly increased and thereafter remained constant in the case of the oxalic acid curve but fell somewhat for the tartaric curve. Thus in these three titrations the extrapolated *E.M.F.*'s of the oxygen–

hydrogen cell were greater at the end of the titration than at the beginning; the actual values are given in Table XI.

TABLE XI.

Acid.	*E.M.F.* of oxygen–hydrogen cell at Beginning.	End.	Difference.
Malonic	1·195	1·228	+0·033
Tartaric	0·828	1·034	+0·206
Oxalic	0·830	0·950	+0·120
Chromic	1·162	1·027	−0·135

The curves in Fig. 3 show that the differences were not proportionally incorporated in the oxygen electrode voltages, but were included mainly in the end-point readings. It was thought that these differences were due simply to a lag in the *E.M.F.*'s of the oxygen electrodes caused by the considerable change in hydrion concentration, which could be overcome by allowing time before taking further readings. When the change was considerable, it was sometimes found that time produced some little effect, but in general, the extrapolated *E.M.F.*'s never fell to the initial values. This change which takes place as the titrated solution attains alkalinity seems to be connected both with the age of the electrodes and with the oxidising nature of the acids. The curve showing the change which took place in the titration of chromic acid is also given in Fig. 3, the actual titration curve being No. 1, Fig. 2, in the previous paper. Although there was no change in the *P.D.* during the first half of the neutralisation, there was a somewhat irregular falling off during the second stage and when the solution had become alkaline it was found that the extrapolated *E.M.F.* was less than the initial value. This occurred in every one of the many titrations undertaken. The hydrogen-ion concentration prevailing during the second half of the titration lay between 10^{-6} and 10^{-7} and it seems that it was here and later in the alkaline solution that the oxidising nature of the chromic acid came into play. No irregularities occurred with the non-oxidising acids dealt with in this paper and especially with malonic acid, the second part of the neutralisation of which was not far removed from the neutral point.

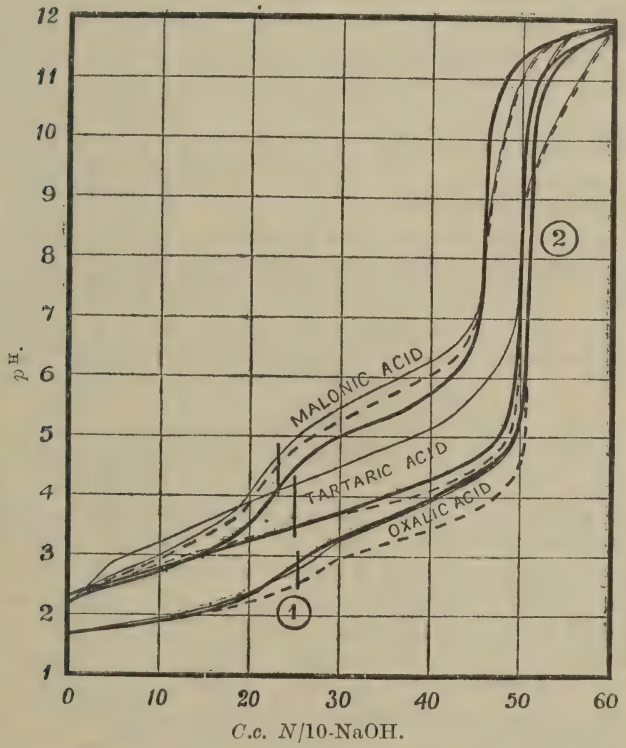
Calibration of the Oxygen Electrode in Titrations.

The erratic behaviour of the oxygen electrode whilst being subjected to rapid changes in hydrion concentration, such as shown in Fig. 3 to take place at the end-points of titrations, renders it almost impossible to affix a satisfactory hydrogen-ion concentration scale to the measured voltages. It is possible, however, to get an approximate idea of the changes in p_H over the greater range of the

itration, for which purpose the following two schemes of calibration ıave been examined.

First, knowing the p_H's of solutions at two remote stages of a itration and the corresponding voltages given by the oxygen elec- rode, one assumes that the intermediate p_H's are proportional to he observed *E.M.F.*'s. In Fig. 4, the p_H curves of the three organic ɛids obtained with the hydrogen electrode are given as heavy lines

Fig. 4.



nd the thin line lying near to each one of them is the curve calcu- ıted from the oxygen electrode titration voltages. It will be seen hat the p_H's given by the malonic acid curve are higher by about ·5 unit, due to a lag of 0·033 volt being divided proportionally over he p_H range of the titration, whereas the lag of 0·206 volt shown by he tartaric acid curve causes the oxygen curve to lie higher on the iagram, in some places nearly a whole p_H unit, and yet in the ase of oxalic acid, with its lag of 0·120 volt, the oxygen curve is lmost coincident with the hydrogen curve, save for a small deviation ı the middle section. This is due to the gradual increase in the

extrapolated *E.M.F.* which took place throughout the acid zon of the oxalic acid titration.

The second method of calibration was based on the fact, illus trated by Fig. 3, that the oxygen electrode voltages are mor positive than the corresponding hydrogen electrode voltages b approximately a fixed amount, when working over a range of hydrio concentration which does not involve sudden changes, and tha the appreciable variations occur only when a very sharp change i hydrion is encountered. Thus in any one of the present titrations if the p_H's at the beginning and at the end are known, the *E.M.F.*' given by the hydrogen electrode as compared with the norma calomel can be calculated, and thus the *P.D.* of the correspondin oxygen–hydrogen cells can be extrapolated. The difference betwee the initial and the final values may then be assumed to have bee introduced at that stage of the titration where the addition of a fe drops of alkali caused a considerable change in the observed *E.M.F* This difference is then added to or subtracted from, as the case ma be, those readings which were taken after the marked change ha taken place. To the titration readings which have thus been adjusted the hydrogen-ion concentration scale may be found by proportion or by what amounts to the same thing, from the formula: Observe *E.M.F.* = Initial extrapolated *P.D.* of the oxygen–hydrogen ce

$$+ 0{\cdot}283 + 0{\cdot}0577 \log 1/[H^{\cdot}].$$

For example, suppose that all that was known of the tartaric aci titration was the initial p_H, 2·29, and the p_H when 60 c.c. of alka had been added, *viz.*, 11·75. The oxygen electrode compared wit the normal calomel gave + 0·413 and + 0·073 volt respectively and from the known p_H's it is calculated that the *E.M.F.* of th hydrogen electrode against the normal calomel would have bee − 0·415 volt at the beginning and − 0·961 volt at the end. Henc the extrapolated *P.D.* of the oxygen–hydrogen cell increased fro + 0·413 −(−0·415) = 0·828 volt to + 0·073 − (− 0·961) = 1·03 volt in the course of the titration, a difference of 0·206 volt. Thi is a considerable quantity to be divided proportionally over th whole titration as was done in the first method of calibration, an consequently would produce a very unsatisfactory hydrion scal But, as Fig. 3 shows, the greater part of this difference was intro duced at the end-point. Therefore, if the difference 0·206 volt b added to each of the voltages observed after the end-point had bee passed and then either a proportional scale be affixed or calculate from $E = 0{\cdot}828 + 0{\cdot}283 + 0{\cdot}0577 \log 1/[H^{\cdot}]$, a more satisfactor calibration is obtained, save for that part of the curve correspondin to the initial alkaline solutions. The curves obtained by thi procedure are given by dotted lines in Fig. 4. The tartaric aci

curve is nearly coincident with the one obtained by the hydrogen electrode, and the malonic acid curve lies closer to the true curve. The oxalic curve, however, is less satisfactory.

In conclusion, it seems that, provided the substances being titrated are not oxidising agents, the second method of calibration leads to the more satisfactory results; when oxidising agents are involved, as, for example, chromic acid, the first method is probably more satisfactory.

Summary.

(1) Oxalic, malonic, succinic, and tartaric acids and dextrose have been titrated electrometrically at 18°. The four acids produce in the course of their neutralisation hydrogen-ion concentrations which extend over the whole acid zone, and therefore partly neutralised solutions may be used for reference purposes in colorimetric determinations of p_{H}.

(2) The dissociation constant of dextrose as a monobasic acid has been found.

(3) Formulæ have been derived for the calculation of the dissociation constants of dibasic acids from the hydrogen electrode titration curves.

(4) The formulæ derived by Auerbach and Smolczyk have been shown to give less accurate results.

(5) Auerbach and Smolczyk's identity, $K_1K_2 = h^2$, where h is the hydrion concentration at the mid-point of the titration curve of a dibasic acid, has been shown to be erroneous.

(6) Attempts have been made to use the oxygen electrode for the purpose of indicating hydrion concentrations in titrations.

The author desires to take this opportunity to thank the Department of Scientific and Industrial Research for a personal grant, and also Prof. J. C. Philip, F.R.S., for facilities for carrying out this work.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, May 26th*, 1925.]

CCLVII.—*Researches on Residual Affinity and Co-ordination. Part XXIV. Heats of Chelation of Dithiolated Metallic Halides.*

By GILBERT T. MORGAN, SYDNEY RAYMOND CARTER, and WILLIAM FINNEMORE HARRISON.

WHEN present in organic thioethers, bivalent sulphur exhibits residual affinity to a remarkable extent so that dialkyl sulphides

combine additively with many metallic halides, giving rise to thiolated co-ordination compounds such as $2Me_2S,SnCl_4$ (Werner and Pfeiffer, *Z. anorg. Chem.*, 1898, **17**, 101), Me_2S,CdI_2 (Werner, *ibid.*, 1897, **15**, 14), $[2Me_2S,PtCl_2]$ and $[Pt,4Me_2S]PtCl_4$ (Tschugaev and Subbotin, *Ber.*, 1910, **43**, 1200). Increased stability is acquired by these thiolated metallic halides when the sulphur is present in a chelate group as in dimethyldithiolethylene, $CH_3{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_3$, a substance which functions as two associating units giving rise by implication of the metallic atom to co-ordination complexes containing one or more five-membered rings (formulæ I, II, and III).

In a previous communication (J., 1922, **121**, 2882) attention was directed to the coincidence that metallic radicals yielding the characteristic insoluble sulphides of analytical practice also give rise to well-defined co-ordination compounds with thioethers. The selective affinity between metal and sulphur is manifested in a similar manner whether in sulphide formation or in the production of thiolated metallic salts.

Moreover, in the case of metals of variable valency, both these modes of combination between metallic radical and sulphur afford an insight into the relative stabilities of the electronic structures of the metallic atoms corresponding with these valency changes.

Copper and gold, which fall into a natural family of univalent metals, have the fundamental electronic structures of Cu^{I} = 2,224,22446,**1** and Au^{I} = 2,8,18,32,18,**1** with single valency electrons. But in their cupric and auric salts the two metals exhibit alternative electronic structures, Cu^{II} = 2,224,22445,**2** and Au^{III} = 2,8,18,32,16,**3** with two and three valency electrons respectively as displayed in cupric and auric salts. In their combinations with sulphur, there is a marked tendency to revert to the lower state of valency, that is, to change from the alternative to the fundamental electronic structure. When cupric halides combine with dimethyldithiolethylene or with other thioethers the resulting thiolated cupric halides change readily to cuprous derivatives. Similarly, the thiolated auric compounds are unstable and especially sensitive to moisture, which promotes a spontaneous change to thiolated aurous derivatives (*ibid.*, p. 2883).

In the case of mercury, thiolation promotes an exaltation of valency (*ibid.*, p. 2884) corresponding with a change from the less stable electronic structure of univalent mercury, Hg^{I} = 2,8,18,32,18,1,**1** to the more stable electronic structure of the bivalent metal, Hg^{II} = 2,8,18,32,18,**2**, which is characteristic of its natural position among the chemical elements.

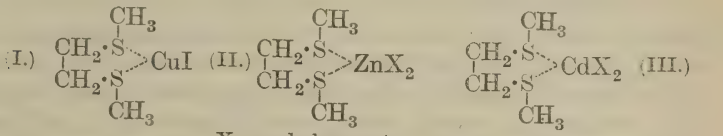
During these earlier investigations it was noticed that the formation of certain dithiolated metallic halides was accompanied by

a very appreciable rise of temperature and we have now determined the heats of chelation of fifteen of these co-ordination compounds.

With the same metallic radical it was found that the heat of combination of dithiol and metallic halides varied with the nature of the halogen, and missing members of the series were prepared in order to obtain comparative measurements.

Dimethyldithiolethylene cuprous iodide * (I), is a pale yellow substance stable in air and only slowly attacked by boiling water.

The zinc series was completed by the production of *dimethyldithiolethylene zinc chloride* and *iodide* (II), the bromide having been already described, and *dimethyldithiolethylene cadmium chloride* and *bromide* (III) were also prepared.



X = a halogen atom.

The thermal measurements described in this paper show how very vague is the former division of chemical substances into atomic and molecular compounds.

Heats of reaction do not represent exactly the free energy of change involved in building up a substance from its simpler components, and cannot, therefore, in the case of these thiolated derivatives, represent the work actually done by residual affinity, but since in many cases the free energy changes are not very different from total energy changes, a certain degree of approximation may be expected. Thus not only the free energy but also the bound energy may be assumed to have some relation to chemical structure.

The heat of chelation of cupric chloride by dimethyldithiolethylene is +14·85 Cals., whereas the heat of formation of cupric sulphide is +9·93 Cals. On the other hand, the more stable cuprous sulphide is formed with the generation of 18·26 Cals., whereas the dithiolated cuprous iodide has a heat of chelation of +5·9 Cals.

The influence of the halogen on the heat of chelation of the dithiolated metallic halides is demonstrated by a study of the complete series of mercury compounds; the data for the chloride, bromide, and iodide are in the descending order of +13·23, +11·33, and +4·83 Cals. In the case of the most exothermic of these three

* *Erratum.*—In the copper compounds each copper atom becomes associated with one molecular proportion of dithiol. The name of the cupric derivative (J., 1922, **121**, 2887) should be *dimethyldithiolethylene cupric chloride*; the prefix *bis* refers to a double molecule as in the preceding dithiolated cuprous bromide.

changes, the value exceeds appreciably that of the heat of formation of mercuric sulphide (10·75 Cals.). The three dithiolated cadmium halides give the series: chloride +12·16 Cals., bromide +11·27 Cals., and iodide +9·96 Cals., these values being all lower than the heat of formation of cadmium sulphide (34·36 Cals). It is of interest to compare the heats of chelation of this dithiolated series with the heats of co-ordination of the cadmium halides with ammonia; the latter values are as follow: $CdCl_2,2NH_3$, 37·24 Cals.; $CdBr_2,2NH_3$, 35·2 Cals.; $CdI_2,2NH_3$, 29·6 Cals. (Tassily, *Ann. Chim. Phys.*, 1899, **17**, 38).

A discrepancy was observed in the case of the dimethyldithiolethylene zinc halides, where the values were chloride, 13·21 Cals. (87°); bromide, 15·35 Cals. (79°); and iodide, 14·23 Cals. (71°), the value obtained for the bromide derivative being the highest of the three (heat of formation of zinc sulphide+41·3 Cals.).

The zinc halides also combine with methylamine to give co-ordination compounds having the general formula $ZnX_2,5NH_2{\cdot}CH_3$ (Ephraim and Linn, *Ber.*, 1913, **46**, 3742), and for these the heats of co-ordination are chloride, 12·79, bromide, 12·48, and iodide, 12·17 Cals., a diminishing series resembling the values obtained with the dithiolated cadmium and mercuric halides. However, in their combinations with ammonia (Isambert, *Compt. rend.*, 1878, **86**, 968; André, *Ann. Chim. Phys.*, 1884, **3**, 66; Tassily, *loc. cit.*) the zinc halides give the following heats of co-ordination: $ZnCl_2,4NH_3$, 68·0 Cals.; $ZnI_2,4NH_3$, 73·95 Cals.; $ZnBr_2,5NH_3$, 82·2 Cals. The ammoniated zinc bromide is anomalous both in composition and in its heat of co-ordination.

The maximum heat of chelation was observed in the case of dithiolated stannic chloride and the next highest value was noted with the corresponding bromide, the values for these two co-ordination compounds, $CH_3{\cdot}S{\cdot}C_2H_4{\cdot}S{\cdot}CH_3,SnX_2$, being 28·06 and 19·40 Cals., respectively. Stannic iodide does not yield a chelated compound, for in this combination two molecular proportions of the iodide combine with one of the dithiol, $CH_3{\cdot}S{\cdot}C_2H_4{\cdot}S{\cdot}CH_3,2SnI_4$. Nevertheless even in this case the heat of co-ordination is very considerable, being 16·58 Cals.

A heat of co-ordination of +12·0 Cals. was observed in the combination of 3 mols. of dimethyldithiolethylene with 2 mols. of bismuth iodide to form the bright scarlet complex,

$$3CH_3{\cdot}S{\cdot}C_2H_4{\cdot}S{\cdot}CH_3,2BiI_3.$$

The following table summarises the calorimetric results obtained for the heats of chelation or co-ordination, in large calories, of the fifteen dithiolated metallic halides; the heats of formation of the corresponding metallic sulphides recorded in Landolt-Börnstein

" Physikalisch-Chemische Tabellen," 1912, based on the work of Berthelot (B) and Thomsen (T), are also included.

Metal.	Dithiolated. Chloride.	Bromide.	Iodide.	Sulphide.
Copper (ic)	+14·85	—	—	+9·93 (Mean B and T)
Copper (ous)	—	—	+5·88	18·26 (T)
Zinc	13·21	+15·35	14·23	41·28 (Mean B and T)
Cadmium	12·16	11·27	9·96	34·35 (T)
Mercury	13·23	11·33	4·83	10·6 (B)
Tin	28·06	19·40	16·58	—
Bismuth	—	—	12·0	—

Experimental.

I. *Preparation and Purification of Dimethyldithiolethylene.*

Dimethyldithiolethylene, prepared by the action of sodium mercaptide on ethylene dibromide (Morgan and Ledbury, J., 1922, **121**, 2882), was purified through the characteristic dithiolated nickel thiocyanate, $Ni(CNS)_2,2CH_3{\cdot}S{\cdot}C_2H_4{\cdot}S{\cdot}CH_3$ (Tschugaev and Kobljamski, *Ber.*, 1908, **41**, 2222). This compound crystallised from 85% alcohol in blue needles which were dried and distilled in steam. The colourless disulphide which separated from the distillate then boiled at 182·5°/750 mm.

II. *Preparation of Dithiolated Metallic Halides.*

Dimethyldithiolethylene Zinc Chloride.—Dry chlorine was passed into a suspension of zinc dust in anhydrous ether and the disulphide was added to the filtered ethereal solution; the white dithiolated compound then separated in crystalline form, melting at 131—132° to a clear liquid. It was very unstable in a moist atmosphere and was immediately decomposed by cold water with liberation of the disulphide (Found: Zn, 25·1; Cl, 27·3; S, 24·4. $C_4H_{10}Cl_2S_2Zn$ requires Zn, 25·3; Cl, 27·45; S, 24·8%. This zinc compound was only slightly soluble in ether but very soluble in acetone; it dissolved in alcohol with decomposition.

Dimethyldithiolethylene zinc iodide was distinctly less affected by moisture than the corresponding chloride or bromide (*ibid.*, p. 2888). Zinc dust (2 g.) and iodine (6 g.) were combined in dry ether and 1 g. of the disulphide was added to the filtered solution; small, white crystals then separated, melting at 169—170° to a clear liquid (Found: Zn, 14·6; I, 57·3; S, 14·4. $C_4H_{10}I_2S_2Zn$ requires Zn, 14·8; I, 57·5; S, 14·5%). The compound was very soluble in acetone and slightly soluble in ether; it dissolved readily in methyl and ethyl alcohols with slight decomposition on boiling, but was only sparingly soluble in other solvents.

Dimethyldithiolethylene Cadmium Chloride.—On addition of the

disulphide to a solution of anhydrous cadmium chloride in dry alcohol, a white, crystalline compound separated, which was very soluble in warm alcohol and crystallised from this solvent in colourless needles; it did not melt below 285° (Found: Cd, 36·95; Cl, 23·2; S, 20·85. $C_4H_{10}Cl_2S_2Cd$ requires Cd, 36·8; Cl, 23·2; S, 21·0%). The thiolated compound was readily soluble in methyl alcohol but almost insoluble in acetone; it was slowly decomposed by cold water.

Dimethyldithiolethylene cadmium bromide, prepared in a similar manner to the preceding compound, had similar properties but did not melt below 285° (Found: Cd, 28·3; Br, 40·7; S, 16·4. $C_4H_{10}Br_2S_2Cd$ requires Cd, 28·5; Br, 40·5; S, 16·2%). The dithiolated cadmium bromide was readily soluble in acetone, ether, or methyl alcohol.

Dimethyldithiolethylene Cuprous Iodide.—A solution of copper sulphate in water was saturated with sulphur dioxide and on the addition of the organic disulphide and potassium iodide, a pale yellow substance was precipitated which was extracted with a strong solution of potassium iodide to remove any unchanged cuprous iodide. The additive compound was then washed with alcohol and dried in a vacuum desiccator. Insoluble in the ordinary organic media, it was unchanged by cold water but slowly decomposed on boiling, leaving cuprous iodide. It was very stable in air, melting and decomposing at 156°, leaving a black residue (Found: Cu, 20·1; I, 40·3; S, 20·8. $C_8H_{20}I_2S_4Cu_2$ requires Cu, 20·3; I, 40·6; S, 20·5%).

III. *Thermal Measurements.*

Description of Apparatus.—In the following calorimetric measurements the two reacting liquids were placed in separate vessels and their temperatures recorded at intervals of a minute; the one reagent was then added to the other, the temperature change being observed. A silver calorimeter of half a litre capacity was used in those cases where the metal was unattacked by the reagents. In the experiments with mercury salts a thin-walled glass calorimeter was employed. The stirrer, which consisted of two rings of sheet nickel, each perforated with eight holes and connected by nickel rods, was raised and lowered about sixty times a minute. The second liquid, contained in a tap funnel, was stirred with a small glass propeller stirrer.

The experimental methods based on the former work (Morgan and Ledbury, *loc. cit.*) were frequently modified in order to obtain reactions of a speed suitable for thermal measurements. In the case of the more stable additive compounds, the thermal data were obtained in the formation of the co-ordination compounds. For

the less stable dithiolated derivatives it was more convenient to prepare the compounds first and subsequently to determine their heats of dissociation.

Dimethyldithiolethylene cupric chloride. This compound is immediately decomposed by a large excess of water. About 2 g. of the substance were decomposed in a calorimeter and the fall in temperature was measured. The heat of dissociation was −3·77 Cals. The heat of solution of cupric chloride in water (1 : 600 water, which was the concentration employed) is given as +11·08 Cals. (Thomsen, *J. pr. Chem.*, 1875, **12**, 276). The heat of reaction of cupric chloride and the disulphide is +14·85 Cals.

Dimethyldithiolethylene cuprous iodide. Potassium iodide solution was added to a solution of copper sulphate (2·2%) and the disulphide and the resulting temperature change compared with a blank experiment in which the disulphide was absent. The difference, which gives the heat of reaction of cuprous iodide and the disulphide, was +5·88 Cals.

Dimethyldithiolethylene zinc chloride. This dithiolated chloride was decomposed with water and the heat of dissociation found to be +2·44 Cals. The heat of solution of zinc chloride (1 : 300) is given by Thomsen as +15·63 Cals. (*J. pr. Chem.*, 1875, **11**, 410). This gives the heat of reaction of zinc chloride and disulphide as +13·19 Cals.

Dimethyldithiolethylene zinc bromide (*loc. cit.*, p. 2888) was treated as in the preceding case. The heat of dissociation was −0·324 Cal. The heat of solution of zinc bromide in water is given by Thomsen as +15·03 Cals. (*J. pr. Chem.*, 1877, **16**, 328); hence the heat of reaction is +15·35 Cals.

Dimethyldithiolethylene zinc iodide. The heat of dissociation with water was −2·87 Cals., the heat of solution of zinc iodide in water (1 : 400) is +11·31 Cals. (Thomsen, *ibid.*, 1877) and hence the heat of reaction of zinc iodide and the disulphide is +14·18 Cals.

Dimethyldithiolethylene cadmium chloride. The cadmium compounds were all decomposed with 2% hydrochloric acid. The specific heat of such a solution is 0·9650 (Marignac, *Ann. Chim. Phys.*, 1876, **8**, 410). The heat of dissociation was −9·15 Cals. The heat of solution of cadmium chloride in water (1 : 400) is +3·01 Cals. (Thomsen, *ibid.*, 1875). Hence the heat of reaction of the dithiol with cadmium chloride is +12·16 Cals.

Dimethyldithiolethylene cadmium bromide. The heat of dissociation was −10·83 Cals.; the heat of solution of cadmium bromide in water (1 : 400) (Thomsen, *ibid.*, 1877) is +0·44 Cal., and hence the heat of reaction is +11·27 Cals.

Dimethyldithiolethylene cadmium iodide. The heat of dissociation was −10·92 Cals. The heat of solution of cadmium iodide in water (1 : 400) is −0·96 Cal. (Thomsen, *ibid.*, 1877). Accordingly, the heat of reaction of cadmium iodide and the disulphide is +9·96 Cals.

Dimethyldithiolethylene mercuric chloride. The heat of reaction was directly measured by the addition of the disulphide to a 3% solution of mercuric chloride in water. The specific heat of such a solution is given by Blümcke as 0·96 (*Ber.*, 1884, **17**, 555). The heat of reaction was +13·23 Cals.

Dimethyldithiolethylene mercuric bromide. A weighed amount of the disulphide was added to an alcoholic solution of mercuric bromide. The heat of solution of mercuric bromide in alcohol was ascertained to be negligible. The heat of reaction was thus found to be +11·33 Cals.

Dimethyldithiolethylene mercuric iodide. Excess of the disulphide was added to a solution of mercuric iodide in alcohol. The heat of reaction was +6·93 Cals. The heat of solution of mercuric iodide in alcohol, which was difficult to determine owing to very sparing solubility, was found to be about −2·1 Cals. Thus the heat of reaction of mercuric iodide and the disulphide is +4·83 Cals.

Trisdimethyldithiolethylene dibismuthotri-iodide. Into a solution of bismuth oxychloride in dilute hydrochloric acid about 1 g. of the disulphide was introduced. Then a solution of about one-third of the theoretical quantity of potassium iodide was added, when the characteristic red compound was formed. The heat of reaction was +35·6 Cals. and correcting for the side reactions this gives a result of +12·0 Cals. for the heat of reaction of bismuth iodide and the disulphide.

Dimethyldithiolethylene stannichloride. For the thermal measurements of the dithiolated tin compounds the copper calorimeter employed was tinned internally. A solution of the disulphide in carbon tetrachloride was run into a solution of stannic chloride in the same solvent, the co-ordination compound being insoluble in this medium. The heat of reaction was +26·98 Cals. The heat of solution of stannic chloride in the solvent was difficult to determine owing to the very hygroscopic nature of the chloride and the resulting rise in temperature. The hydration effects were minimised by leading dry carbon dioxide above the calorimeter liquid and placing fused calcium chloride between the ebonite lids; readings were taken every 15 seconds. The heat of solution (1 g. of stannic chloride to 300 g. of carbon tetrachloride) was +0·870 Cal. The heat of solution of the disulphide in the solvent was +0·232 Cal. The specific heat of carbon tetrachloride was taken as 0·2014

(Mills and MacRae, *J. physical Chem.*, 1895, **9**, 360). Correcting for the heats of solution of the reacting substances, a value of +28·06 Cals. is obtained for the heat of reaction of stannic chloride and the disulphide.

Dimethyldithiolethylene stannibromide. The heat of reaction of the bromide and disulphide, both in carbon tetrachloride solution, was +22·32 Cals. The heat of solution of stannic bromide in carbon tetrachloride was found to be —3·15 Cals. (1 g. of stannic bromide to 100 g. of carbon tetrachloride). The heat of solution of disulphide in carbon tetrachloride is +0·232 Cal.

$$C_4H_{10}S_2 + SnBr_4 \longrightarrow C_4H_{10}S_2,SnBr_4 + 19{\cdot}40 \text{ Cals.}$$

Dimethyldithiolethylene stanni-iodide. By adopting the foregoing method the reaction was not complete using the common organic solvents. Finally a solution of stannic chloride in carbon tetrachloride was added to a solution of dimethyldithiolethylene stanni-iodide in carbon tetrachloride; dimethyldithiolethylene stanni-chloride and free stannic iodide were then produced. Nearly twice the theoretical quantity of stannic chloride was necessary to complete the chemical change.

$$\underset{\text{soln.}}{C_4H_{10}S_2,2SnI_4} + \underset{\text{soln.}}{SnCl_4} \longrightarrow C_4H_{10}S_2,SnCl_4 + \underset{\text{soln.}}{2SnI_4} + 30{\cdot}30 \text{ Cals.}$$

$$\underset{\text{soln.}}{C_4H_{10}S_2} + \underset{\text{soln.}}{SnCl_4} \longrightarrow C_4H_{10}S_2,SnCl_4 + 26{\cdot}98 \text{ Cals.}$$

$$\text{Hence, } \underset{\text{soln.}}{2SnI_4} + \underset{\text{soln.}}{C_4H_{10}S_2} \rightarrow \underset{\text{soln.}}{C_4H_{10}S_2,2SnI_4} - 3{\cdot}3 \text{ Cals.}$$

The heat of solution of stannic iodide in carbon tetrachloride (1 : 200) was found to be —3·81 Cals. The heat of solution of dimethyldithiolethylene stanni-iodide in carbon tetrachloride (1 : 200) was —27·27 Cals. The heat of solution of the disulphide in carbon tetrachloride (1 : 200) was +0·232 Cal. Hence the heat of reaction of the disulphide and stannic iodide is +16·58 Cals.

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CCLVIII.—*The Rotatory Dispersion of Derivatives of Tartaric Acid. Part II. Acetyl Derivatives.*

By Percy Corlett Austin and James Ritchie Park.

The effect produced on the character of the rotatory dispersion of tartaric acid by bridging across various hydroxyl groups with methylene (Austin and Carpenter, J., 1924, **125**, 1939) was so remarkable that an investigation of other types of bridging became desirable. Condensation of the carboxyl groups with production of an anhydride ring is readily effected if the alcoholic groups are acetylated at the same time (Chattaway and Parkes, J., 1923, **123**, 663). Diacetyltartaric anhydride is dextrorotatory in solution in acetone or benzene and lævorotatory in alcohol or water (Anschütz and Pictet, *Ber.*, 1880, **13**, 1178; Pictet, *Arch. Sci. phys. nat.*, 1882, **7**, 82; Freundler, *Ann. Chim. Phys.*, 1895, **4**, 242), but the data recorded show considerable variations. Freundler states that whereas the rotations of dibenzoyltartaric anhydride in solution in acetone are practically independent of concentration, this is not the case with the diacetyl compound. He points out, however, that some of the solutions examined show mutarotation.* It seemed desirable, therefore, to study the compound in detail.

The Cause of the Mutarotation of Diacetyltartaric Anhydride.

We have found that if special care is taken to eliminate moisture, solutions of diacetyltartaric anhydride in acetone or ethyl acetate do not exhibit mutarotation and the strong dextrorotations are permanent. The rotations conform to the requirements of the law of "simple" rotatory dispersion (compare Austin and Carpenter, *loc. cit.*; Lowry and Cutter, this vol., p. 604). This led us to surmise that the variations in the values of the specific rotation with changes of concentration which were recorded by Freundler might also be due to the presence of moisture in the solvent. *This we have verified experimentally.* It is therefore clear that when a dry solvent is used the two principal anomalies which are characteristic of tartaric acid and of many of its derivatives, *viz.*, anomalous rotatory dispersion and sensitiveness of rotatory power to changes of concentration, disappear simultaneously.

On adding water to the dry solutions, a change of rotation soon became apparent, the rate of change increasing with the amount of water present; with one and with four molecular proportions of water, final steady values were reached after about $1\frac{1}{2}$ days

* The values given by Freundler for specific rotations are obviously intended to represent molecular rotations.

and 16 days, respectively. The fact that this mutarotation is due to the hydrolysis of the anhydride ring and not to an isomeric change catalysed by the water (compare Lowry, this vol., p. 1376) was proved by isolating pure *diacetyltartaric acid* from solutions in which mutarotation was complete. The final readings were strongly lævorotatory, but the values depended on the amount of water used, as is shown in Table I.

TABLE I.

Influence of Water upon the Rotatory Power of Diacetyltartaric Acid in Acetone at 20°.

Ten g. of $C_8H_8O_7$ (anhydride) in 100 c.c. $l = 4$.

Mols. of H_2O.	α_{5780}.	α_{5461}.	α_{4359}.	Mols. of H_2O.	α_{5780}.	α_{5461}.	α_{4359}.
1	−11·23°	−13·12°	−26·43°	4	−13·10°	−15·26°	−30·31°
2	−12·18	−14·10	−28·27	5	−13·56	−15·68	−31·13
3	−12·91	−14·93	−29·29	12	−14·61	−17·00	−33·20

The cause of this increase of lævorotation with increasing amounts of water has not yet been determined. It may be due (i) to association with water molecules or (ii) to ionic dissociation of the diacetyltartaric acid. That some such influence is involved can be inferred from a study of the velocity coefficients (Table V).

The Formation of Diacetyltartaric Acid.

The results shown in Table I left us in doubt as to the true value of the rotatory power of diacetyltartaric acid until the latter substance had been isolated and identified. The purification of the acid was a somewhat troublesome process, since we were long unable to obtain any definite crystals from the solutions. Moreover, the data in reference to the properties of this acid were very meagre. Rochleder, who appears to have been the first to obtain crystals of the acid (*Sitz. Ber. Akad. Wiss. Wien*, 1859, **29**, 26), merely states that it is deliquescent; he gives neither analysis nor melting-point. W. H. Perkin, sen. (J., 1867, **20**, 138), describes the acid as a transparent, gum-like substance, whilst Colson (*Compt. rend.*, 1892, **114**, 177) obtained deliquescent crystals of a lævorotatory compound, melting at 58° and corresponding with the formula $C_8H_{10}O_8,3H_2O$. This substance we have been unable to obtain; but we have separated from solutions in benzene large, soft crystals, containing benzene of crystallisation (1½ mols.). The benzene was easily driven off by heat; the residual white powder melted at 118° and was the anhydrous acid, $C_8H_{10}O_8$. A solution of this in dry acetone was strongly lævorotatory and its rotatory dispersion was also simple. Moreover, its molecular

rotatory power was identical with that calculated from the final readings after mutarotation, when one molecular proportion of water was used. Thus, when the anhydride and water are mixed in equimolecular proportion in the presence of acetone, hydrolysis of the anhydride is complete in about 16 days and the exaltation of the lævorotation in the presence of more water must be due to some other cause.

Since the simple salts of tartaric acid have been proved to exhibit complex rotatory dispersion (Lowry and Austin, Bakerian Lecture, *Phil. Trans.*, 1922, *A*, **222**, 249), this is the first instance of simple rotatory dispersion in the tartaric acid series, which is independent of any ring formation. Even more important, however, is the fact that the anomalies have been eliminated by replacing the hydroxylic hydrogen atoms by acyl groups without bridging, whereas the substitution of alkyl groups for the carboxylic hydrogen atoms is known to be without effect.

We may therefore conclude that *the alcoholic hydroxyl groups are important, though possibly not essential factors, in the development of anomalous rotatory dispersion in tartaric acid* (compare Lowry and Austin, *Nature*, 1924, **114**, 431).

Anomalous Rotatory Dispersion caused by the Superposition of Opposite Partial Rotations.

(*a*) An interesting feature of the mutarotation of diacetyltartaric anhydride is the development of anomalous rotatory dispersion during the transition from the simple dispersion of the dextrorotatory anhydride to the simple dispersion of the lævorotatory acid. This is clearly shown in Fig. 1 and is a striking vindication of Arndtsen's hypothesis in reference to the origin of the anomalous rotatory dispersion of tartaric acid (*Ann. Chim. Phys.*, 1858, **54**, 421; Lowry and Austin, *Phil. Trans.*, *loc. cit.*; Lowry and Cutter, this vol., p. 607).

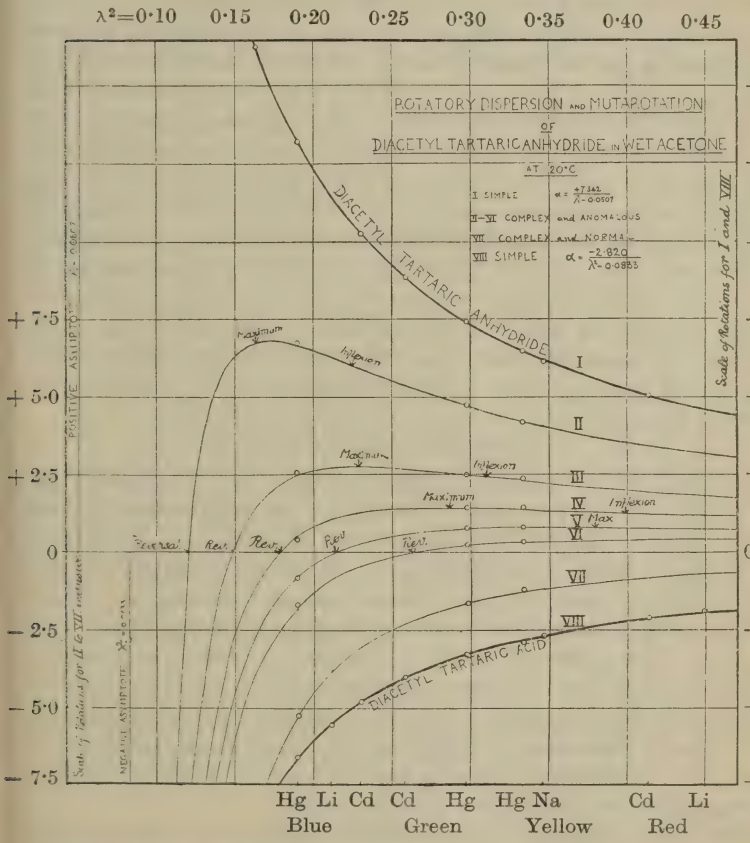
It is an essential feature of this hypothesis that the two compounds the partial rotations of which are superposed, in order to produce an anomalous dispersion, must not only be opposite in sign but of unequal dispersion. This condition is fulfilled in the present instance, since, whilst the anhydride has a dispersion-constant $\lambda^2 = 0{\cdot}0507$, the acid has a dispersion-constant $\lambda^2 = 0{\cdot}0833$, the lævo-component being the more dispersive (see Table V) just as in the case of tartaric acid and its esters (Lowry and Austin, *loc. cit.*) and of the two methylene derivatives (Austin and Carpenter, *loc. cit.*).

The figure shows the curves of simple dispersion representing the anhydride (I) and the acid (VIII) respectively together with six

intermediate curves, which are plotted on a larger vertical scale in order to show the anomalies.*

During the course of the mutarotation only the three mercury lines were read, but the form of the dispersion curves can be accurately determined by extrapolation beyond these points, since we know that we are dealing with mixtures of two known components.

FIG. 1.



It will be seen that five of the curves (II—VI) are not only *complex* but also *anomalous*, the positions of the characteristic anomalies being indicated in Table V. No. VII, although still obviously complex (since mutarotation is incomplete), is *normal*, as are also all

* The characteristic anomalies are (i) reversal of sign, λ_ρ; (ii) maximum point at λ_μ; and (iii) point of inflexion at λ_σ (Table V). In several instances the actual reversals were observed experimentally for the mercury violet, green and yellow lines in succession.

the curves (not shown in the diagram) which lie between Nos. VII and VIII. This follows necessarily from the fact that k_2 has become greater than k_1, whilst λ_2^2 is also greater than λ_1^2. Similarly, all curves which lie between I and II must be complex and anomalous.

(*b*) A change of a very similar character was observed when a solution of the anhydride in warm water was cooled to 20°. Hydrolysis of the anhydride was so rapid that the first readings which could be obtained were lævorotatory, but instead of remaining constant they soon began to diminish and a very *slow mutarotation in the opposite direction* to that shown in Fig. 1 took place until eventually only dextrorotations were observed. Thus the simple lævorotatory dispersion gave place to complex and later to anomalous dispersion, the rotation for the yellow mercury line showing reversal of sign after 19 days. This was followed by a reversal in the green after 20 days and in the violet after 32 days (Table VI). This change is obviously due to slow hydrolysis of the acetyl groups with the liberation of dextrorotatory tartaric acid. A similar hydrolysis, which was slower still, was also noticed in the case of the mutarotation of the anhydride in acetone, with twelve molecular proportions of water (p. 1927), after the attainment of the maximum lævorotations.

Experimental.

Diacetyltartaric anhydride was prepared by Chattaway and Parkes's method (*loc. cit.*). Owing to its deliquescent nature, recrystallisation from benzene did not suffice to purify it; eventually very pure specimens were obtained by allowing hot solutions of the compound in acetic anhydride to cool in a desiccator. Traces of the solvent were eliminated by washing with dry ether. The rotations were measured at 20° in solutions in acetone and in ethyl acetate. Both solvents were carefully dried shortly before use by the addition of phosphorus pentoxide, followed by refractionation. The specific rotations in ethyl acetate were considerably lower than those in acetone. Results are set forth in Tables II and III, photographic readings being given in italics.

The Mutarotation of Diacetyltartaric Anhydride in Wet Acetone.—A solution of diacetyltartaric anhydride (10 g.) in dry acetone (nearly 100 c.c.) at 20° was, after the addition of water (0·85 c.c. = 1 mol.), made up to 100 c.c. with dry solvent. The solution was transferred as rapidly as possible into a 4-dcm. tube and readings were taken at intervals measured from the moment when the water was added. Comparison of the final constant readings with those obtained from a solution of an equivalent quantity of the pure acid in dry acetone showed that the reaction was complete

Table II.

The Rotatory Dispersion of Diacetyltartaric Anhydride in Acetone at 20°.

(a) *First Series.* 25 G. of $C_8H_8O_7$ in 100 c.c. of solution.

Length of tube = 4 dcm. $\alpha = [\alpha]$. Simple formula $[\alpha_1] = \frac{+ 18{\cdot}354}{\lambda^2 - 0{\cdot}0507}$. $[M_1] = 2{\cdot}16\alpha$.

	λ.	α = [α] obs.	[α₁] calc.	[α]−[α₁].		λ.	α = [α] obs.	[α₁] calc.	[α]−[α₁].
Li	6708	+45·94°	+45·97°	−0·03°	Cu	5105	+87·45°	+87·44°	+0·01°
Cd	6438	50·49	50·45	+0·04	Cd	5086	88·17	88·25	−0·08
Zn	6364	51·92	51·80	+0·12	Zn	4811	101·50	101·54	−0·04
Li	6104	57·00	57·02	−0·02	Cd	4800	102·00	102·13	−0·13
Na	5893	61·90	61·88	+0·02	Zn	4722	106·49	106·54	−0·05
Cu	5782	64·74	64·71	+0·03	Cd	4678	108·93	109·16	−0·23
Hg	5780	64·75	64·76	−0·01	Li	4602	113·97	113·93	+0·04
Cu	5700	67·05	66·93	+0·12	Hg	4359	131·73	131·75	−0·02
Ag	5469	73·85	73·88	−0·03	*Fe*	*4157*	*150*	*150·3*	*−0·3*
Hg	5461	74·15	74·15	±	*Fe*	*4064*	*160*	*160·3*	*−0·3*
Cu	5219	82·83	82·79	+0·04	*Fe*	*4046*	*162*	*162·4*	*−0·4*
Ag	5209	83·15	83·18	−0·03	*Fe*	*3978*	*171*	*170·6*	*+0·4*
Cu	5154	85·38	85·39	−0·01					

(b) *Second Series.* 10 G. of $C_8H_8O_7$ in 100 c.c. of solution.

Length of tube = 4 dcm. $\alpha = 0{\cdot}4[\alpha]$. Simple formula $[\alpha_1] = \frac{+ 18{\cdot}354}{\lambda^2 - 0{\cdot}0507}$.

	λ.	α.	[α] obs.	[α₁] calc.	[α]−[α₁].		λ.	α.	[α] obs.	[α₁] calc.	[α]−[α₁].
Cd	6438	+20·20°	+50·50°	+50·45°	+0·05°	Cd	5086	35·29°	88·23°	88·25°	−0·02°
Zn	6364	20·72	51·80	51·80	±	Zn	4811	40·61	101·52	101·54	−0·02
Na	5893	24·79	61·97	61·88	+0·09	Cd	4800	40·82	102·05	102·13	−0·08
Cu	5782	25·88	64·70	64·71	−0·01	Zn	4722	42·62	106·55	106·54	+0·01
Hg	5780	25·92	64·80	64·76	+0·04	Cd	4678	43·60	109·00	109·16	−0·16
Cu	5700	26·77	66·93	66·93	±	Hg	4359	52·70	131·75	131·75	±
Ag	5469	29·52	73·80	73·88	−0·08	*Fe*	*4072*	*64*	*160*	*159·4*	*+0·6*
Hg	5461	29·66	74·15	74·15	±	*Fe*	*4046*	*65*	*162·5*	*162·4*	*+0·1*
Cu	5219	33·12	82·80	82·79	+0·01	*Fe*	*3978*	*68·2*	*170·5*	*170·6*	*−0·1*
Ag	5209	33·25	83·13	83·18	−0·05	*Fe*	*3879*	*73·5*	*183·7*	*183·9*	*−0·2*
Cu	5154	34·16	85·40	85·39	+0·01	*Fe*	*3860*	*74·8*	*187*	*186·7*	*+0·3*
Cu	5105	34·97	87·43	87·44	−0·01						

Table III.

The Rotatory Dispersion of Diacetyltartaric Anhydride in Ethyl Acetate at 20°.

8·250 G. of $C_8H_8O_7$ in 100 c.c. of solution.

Length of tube = 4 dcm. $\alpha = 0{\cdot}33[\alpha]$. Simple Dispersion $[\alpha_1] = \frac{+ 12{\cdot}177}{\lambda^2 - 0{\cdot}0570}$.

	λ.	α.	[α] obs.	[α₁] calc.	[α]−[α₁].		λ.	α.	[α] obs.	[α₁] calc.	[α]−[α₁].
Cd	6438	+11·26°	+34·12°	+34·06°	+0·06°	Cu	5105	19·79°	59·97°	59·81°	+0·16°
Zn	6364	11·64	35·27	34·99	+0·28	Cd	5086	19·98	60·54	60·38	+0·16
Na	5893	13·80	41·82	41·95	−0·13	Zn	4811	23·20	70·30	69·80	+0·50
Cu	5782	14·55	44·09	43·91	+0·18	Cd	4800	23·11	70·03	70·22	−0·19
Hg	5780	14·58	44·18	43·95	+0·23	Zn	4722	24·30	73·63	73·37	+0·26
Cu	5700	14·95	45·30	45·45	−0·15	Hg	4359	30·23	91·61	91·55	+0·06
Ag	5469	16·54	50·12	50·30	−0·18	*Fe*	*3978*	*40·0*	*121·2*	*120·3*	*+0·9*
Hg	5461	16·66	50·48	50·48	±	*Fe*	*3720*	*50·0*	*151·5*	*149·6*	*+1·9*
Cu	5219	18·66	56·54	56·54	±	*Fe*	*3609*	*55·0*	*166·7*	*166·2*	*+0·5*
Ag	5209	18·77	56·88	56·81	+0·07						

in about 16 days. Thus, since the proportion of acid to anhydride could be readily calculated at any moment, attempts were made to measure the reaction velocity coefficient. The results (Table IV) show that after a short period of induction (about 10—12 minutes) the reaction approximates more closely to the unimolecular than to the bimolecular type, but the agreement is not wholly satisfactory, since after 2 or 3 days the values of k' fall off rapidly. This fact, taken in conjunction with the gradual increase of lævorotation with increasing amounts of water (Table I), leads us to conjecture that there are probably two reactions taking place simultaneously or consecutively, *viz.* (1) opening of the anhydride ring and (2) association of anhydride or of acid with water. Previous attempts to measure the reaction velocity (Deakin and Rivett, J., 1912, **101**, 127) of this compound by conductivity measurements in aqueous solutions failed on account of the rapidity of hydration of the anhydride. We also made observations of mutarotation with larger amounts of water, but these are reserved for further investigation.

TABLE IV.

The Mutarotation of Diacetyltartaric Anhydride in Wet Acetone at 20°.

10 G. of $C_8H_8O_7$ + 0·85 g. (1 mol.) of H_2O in 100 c.c. of solution.

Length of tube 4 dcm. Values of the velocity coefficients, k' (unimolecular) and k'' (bimolecular), are calculated for $[M]_{5461}$.

Intervals (mins.).	a_{5780}.	a_{5461}.	a_{4359}.	$[M]_{5461}$.	$k' \times 10^6$.	$k'' \times 10^6$.
—	+25·92°	+29·66°	+52·70°	+160·16°	—	—
5	25·81	29·50	—	159·30	746	747
9	25·81	29·50	52·35	159·30	414	415
12	25·75	29·47	—	159·14	369	370
27	25·75	29·22	—	157·79	382	384
60	25·15	28·75	—	155·25	358	362
120	24·40	27·87	49·10	150·50	356	364
180	23·56	26·84	47·65	144·94	378	392
260	22·55	25·55	45·43	137·97	388	409
750	17·10	19·52	33·55	105·41	361	414
990	14·69	16·58	28·88	89·53	369	445
1590	9·13	10·42	16·75	56·27	376	514
2310	4·21	4·75	6·75	25·65	378	603
2700	2·38	2·50	2·50	13·50	373	644
2940	+ 1·41	+ 1·45	+ 0·45	7·83	366	658
3060	+ 0·82	+ 0·75	− 0·75	4·05	368	681
3180	+ 0·29	+ 0·23	− 1·70	+ 1·19	363	682
3690	− 1·35	− 1·64	− 5·22	− 8·86	356	739
4320	− 2·87	− 3·44	− 8·69	− 18·58	344	792
5640	− 5·38	− 6·44	−13·75	− 34·78	329	958
7200	− 7·10	− 8·38	−17·25	− 45·25	305	1114
13 days	−10·91	−12·87	−25·75	− 69·50	274	9081
∞	−11·23	−13·12	−26·43	− 70·85	—	—

The Slow Mutarotation of Diacetyltartaric Acid in Aqueous Solution.—A solution of diacetyltartaric anhydride (10 g.) in warm water was cooled and made up to 100 c.c. at 20°. The anhydride was hydro-

TABLE V.

Molecular Rotation Constants and Anomalies during the Mutarotation of Diacetyltartaric Anhydride.

$$[M] = \frac{k_1}{\lambda^2 - 0{\cdot}0507} - \frac{k_2}{\lambda^2 - 0{\cdot}0833}.$$

Dispersion.	Curve No.	Intervals in hours.	k_1.	k_2.	λ_ρ. Reversal.	λ_μ. Maximum.	λ_σ. Inflexion.
Simple	I	—	39·645	0	—	—	—
Complex and anomalous	II	38½	16·560	8·868	0·3476	0·4151	0·4733
	III	45	14·475	9·669	0·3858	0·4786	0·5565
	IV	49	13·502	10·043	0·4218	0·5363	0·6305
	V	51	12·854	10·292	0·4628	0·6159	0·7118
	VI	53	12·372	10·477	0·5134	0·6783	0·8096
Complex and normal	VII	61½	10·639	11·143	—	—	—
Simple	VIII	∞	0	15·230	—	—	—

lysed almost immediately to diacetyltartaric acid, the first reading (after an interval of 45 minutes) giving a value — 13·36° for Hg_{5461} in a 4-dcm. tube. On standing, slow mutarotation took place, the readings for the mercury yellow, green, and violet lines becoming positive after 19, 20, and 33 days respectively. Thus the rotatory dispersion became anomalous owing to the slow liberation of tartaric acid. Results are set forth in Table VI.

TABLE VI.

The Slow Mutarotation of Diacetyltartaric Acid in Aqueous Solution at 20°.

10 G. of $C_8H_8O_7$ (anhydride) in 100 c.c. of solution. $l = 4$.

Intervals.	a_{5780}.	a_{5461}.	a_{4359}.	Intervals.	a_{5780}.	a_{5461}.	a_{4359}.
45 mins.	−11·43°	−13·36°	−25·79°	31 days	+1·31°	+1·38°	−0·27°
15 hrs.	−10·29	−11·77	−23·32	33 ,,	+1·78	+1·66	+0·36
17¾ ,,	− 9·97	−11·57	−22·79	38 ,,	+1·90	+1·92	+1·07
21¼ ,,	− 9·74	−11·18	−22·02	42 ,,	+2·24	+2·34	+1·43
38¼ ,,	− 8·88	−10·03	−19·92	45 ,,	+2·48	+2·59	+1·64
62½ ,,	− 7·00	− 8·29	−17·22	48 ,,	+2·54	+2·69	+1·88
116 ,,	− 5·07	− 5·96	−11·75	56 ,,	+2·91	+3·13	+2·90
184 ,,	− 3·32	− 3·96	− 9·68	59 ,,	+3·13	+3·34	+3·05
15 days	− 0·69	− 1·00	− 4·79	62 ,,	+3·17	+3·37	+3·37
20 ,,	+ 0·18	− 0·04	− 3·03	71 ,,	+3·48	+3·62	+3·46
26 ,,	+ 0·83	+ 0·81	− 1·37				

The Preparation of Diacetyltartaric Acid, $\begin{matrix} CH_3{\cdot}CO{\cdot}O{\cdot}CH{\cdot}CO_2H \\ | \\ CH_3{\cdot}CO{\cdot}O{\cdot}CH{\cdot}CO_2H \end{matrix}$—

A solution in which mutarotation of the anhydride was complete was allowed to evaporate in a vacuum desiccator. The colourless syrup obtained (in one case only this crystallised on long standing) was dissolved in hot benzene, in which it was only slightly soluble, and the solution was allowed to remain in the desiccator. The soft, large, transparent crystals that formed slowly smelled of benzene and soon became opaque when the solvent was decanted

(Found by titration with KOH : equiv., 174·3. $C_8H_{10}O_8 + 1\frac{1}{2}C_6H_6$ requires equiv., 175·5). When the crystals were heated at 85° for 15—20 minutes and crushed, the smell of benzene was removed (Found : equiv., 116·8. $C_8H_{10}O_8$ requires equiv., 117·0). The substance, m. p. 118°, was therefore pure. A solution in dry acetone containing 10·8336 g. (equivalent to 10 g. of anhydride) in 100 c.c. was lævorotatory and the dispersion simple. The readings corresponded exactly with the final readings obtained in the mutarotation of an equivalent quantity of the anhydride in acetone containing water (1 mol.). The results are set forth in Table VII.

TABLE VII.

Rotatory Dispersion of Diacetyltartaric Acid in Acetone at 20°.

10·8336 G. of $C_8H_{10}O_8$ (equiv. to 10 g. of $C_8H_8O_7$) in 100 c.c. of solution. $l = 4$.

Simple formula $[\alpha_\lambda] = \frac{-6{\cdot}508}{\lambda^2 - 0{\cdot}0833}$ $[M_1] = 5{\cdot}4\alpha$.

	λ.	α.	[α] obs.	[α] calc.	[α]—[α].		λ.	α.	[α] obs.	[α] calc.	[α]—[α].
Li	6708	— 7·72°	—17·81°	—17·75°	—0·06°	Cu	5105	—15·89°	—36·67°	—36·70°	+0·03°
Cd	6438	— 8·52	—19·66	—19·65	—0·01	Cd	5086	—16·07	—37·08	—37·11	+0·03
Zn	6364	— 8·74	—20·17	—20·23	+0·06	Zn	4811	—19·00	—43·84	—43·92	+0·08
Li	6104	— 9·75	—22·50	—22·50	±	Cd	4800	—19·18	—44·26	—44·24	—0·02
Na	5893	—10·65	—24·57	—24·65	+0·08	Zn	4722	—20·15	—46·50	—46·59	+0·09
Cu	5782	—11·21	—25·87	—25·92	+0·05	Cd	4678	—20·84	—48·09	—48·02	—0·07
Hg	5780	—11·23	—25·91	—25·95	+0·04	Li	4602	—22·07	—50·93	—50·65	—0·28
Cu	5700	—11·64	—26·86	—26·93	+0·07	Hg	4359	—26·43	—60·99	—60·99	±
Ag	5469	—13·08	—30·18	—30·15	—0·03	*Fe*	*4132*	*—32·5*	*—75·0*	*—74·4*	*—0·6*
Hg	5461	—13·12	—30·28	—30·28	±	*Fe*	*4046*	*—35*	*—80·8*	*—80·9*	*+0·1*
Cu	5219	—14·89	—34·36	—34·42	+0·06	*Fe*	*3978*	*—37·5*	*—86·5*	*—86·8*	*+0·3*
Ag	5209	—14·98	—34·57	—34·61	+0·04	*Fe*	*3879*	*—42*	*—96·9*	*—96·9*	±
Cu	5154	—15·48	—35·72	—35·69	—0·03						

We are indebted to the Government Grant Committee of the Royal Society for a substantial grant for the purchase of the necessary apparatus. We are also indebted to Prof. T. M. Lowry, C.B.E., F.R.S., for his criticism of this paper.

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CCLIX.—*The Chemistry of Petroleum. Part II. The Action of Sodium Hypochlorite on Sulphur Compounds of the Types found in Petroleum Distillates.*

By STANLEY FRANCIS BIRCH and WOODFORD STANLEY GOWAN PLUCKNETT NORRIS.

THE refining of petroleum distillates by the "hypochlorite process" as advocated by Dunstan and Brooks (*Ind. Eng. Chem.*, 1922, **14**, 1112), which involves the oxidation of the offensive sulphur com-

pounds by means of an alkali hypochlorite, has not only been adopted as a standard method of treating the light distillates from Persian petroleum, but is rapidly becoming more generally used throughout the petroleum industry. For this reason, and more particularly because misleading statements reflecting unfavourably upon the efficiency of this process have appeared in the technical literature, it was of obvious importance to investigate the mechanism of the oxidation. In the present paper we describe the action of sodium hypochlorite solution on petroleum solutions of representative members of the types of sulphur compounds which occur in the soda-washed distillate (see Part I, this vol., p. 898).

Observations relevant to this subject have been made by Waterman and Heimal (*J. Inst. Pet. Tech.*, 1924, **46**, 812). Under the conditions they employed, diphenyl sulphide, ethyl mercaptan, carbon disulphide, diphenylsulphone, diethylsulphone, and ethyl thiocyanate were " completely removed " from petroleum solution, whilst phenyl mercaptan, diethyl sulphide, phenylthiocarbimide, phenylthiocyanate, and diphenyl sulphoxide were " substantially removed." Organic disulphides were not examined, nor were any of the oxidation products investigated. Wood, Lowy, and Faragher (*Ind. Eng. Chem.*, 1924, **16**, 1116) state quite definitely that alkyl sulphides, alkyl disulphides, and thiophen are not attacked by sodium hypochlorite solution. They also state that mercaptans are simply converted into the disulphides, which remain dissolved in the solvent employed; that they obtained no evidence of chemical action between the aqueous reagent and free sulphur, sulphoxides, or sulphones; and that hydrogen sulphide is oxidised to free sulphur and water, whilst carbon disulphide is converted into sodium carbonate and sodium sulphate.

The discrepancies between the two sets of results have made it necessary to investigate the subject anew.

It may be stated at once that all the mercaptans, organic sulphides, and organic disulphides which we have examined are quantitatively oxidised by sodium hypochlorite, the reaction proceeding quite readily provided a suitably active solution is employed, whilst thiophen and elementary sulphur remain unattacked.

The greater the tendency of a solution of sodium hypochlorite to decompose spontaneously the greater, naturally, will be its reactivity towards oxidisable compounds. Kaufmann (*Z. angew. Chem.*, 1924, **37**, 364), who considers the active agent in hypochlorite solutions to be free hypochlorous acid, $OCl' + H_2O \rightleftharpoons HOCl + OH'$, has shown that the velocity of spontaneous decomposition of aqueous sodium hypochlorite is inversely proportional to the concentration of hydroxyl ions, and that the fraction of the

total hypochlorite ions destroyed in unit time is independent of the actual concentration of hypochlorite. Thus the reactivity of a solution of sodium hypochlorite should be increased by dilution and decreased by the addition of free alkali, conclusions which have been independently reached in studying the interaction of this reagent and various compounds of sulphur. It is for this reason that, in stating certain derivatives of sulphur to be readily oxidised by hypochlorite, we have also stated that the latter must be " suitably active."

The organic solvent used was a special fraction of petroleum, b. p. 100—175°, which had been freed from aromatic compounds by shaking with a large excess of concentrated sulphuric acid, and afterwards thoroughly washed with a solution of sodium hypochlorite ; the sulphur content was thereby reduced below 0·005%.* To the petroleum thus purified, the various sulphur compounds were added in amounts sufficient to give solutions containing from 0·6% to 0·9% S. The solutions of sodium hypochlorite were prepared by leading chlorine into an aqueous solution of pure sodium hydroxide until the free alkali had been reduced to a predetermined amount ; greater alkali content could then be obtained by adding solid sodium hydroxide, without appreciably altering the amount of available chlorine. The latter was determined by adding acetic acid and potassium iodide and titrating the liberated iodine. For the estimation of free alkali, the hypochlorite was first decomposed by boiling with hydrogen peroxide ; the cooled liquid was then titrated with hydrochloric acid, with methyl-orange as indicator, and, the quantity of sodium carbonate being quite small, the result calculated as sodium hydroxide (*vide infra*, p. 1942).

It was usual to shake 25 c.c. of the analysed reagent with 25 c.c. of the standard solution of sulphur compound in a bottle closed by means of a cork covered with tin-foil. A mechanical shaker was used, the speed being maintained constant throughout this research. After a period of shaking previously decided upon, the petroleum layer and the aqueous liquid were separated, and analysed.

Organic Sulphides.

Since no complication arises from the formation of acidic oxidation products, it is convenient to consider first the interaction of aqueous

* All estimations of sulphur in petroleum were carried out by means of the lamp method.

We wish here to thank Miss G. E. Hickes and Mr. D. Carter, of the Analytical Department, for carrying out the numerous estimations which this research has entailed.

sodium hypochlorite and a petroleum solution of an organic sulphide. The latter is converted quantitatively into the corresponding sulphone. Not even traces of any intermediate compound (*i.e.*, a sulphoxide) could be isolated, nor does hypochlorite appear to exert any further action on sulphones; in fact, the available chlorine used up generally corresponds very closely with four atoms per atom of sulphur oxidised. The reagent does not become appreciably less alkaline during this reaction.

Kahlbaum's diethyl, di-*n*-propyl, di*iso*butyl, and di*iso*amyl sulphides were employed without further purification. In the case of diethyl sulphide, at the conclusion of the reaction, the aqueous liquid was evaporated and the residue extracted with chloroform; the diethylsulphone, m. p. 70°, obtained from the extract in 75% yield, was identified by comparison with a genuine specimen. The higher sulphones, which are more soluble in petroleum than in water, were prepared in yields of over 70% by shaking the corresponding sulphides with aqueous sodium hypochlorite alone; the resulting oils were taken up in chloroform, and after drying over calcium chloride, the solvent was removed, and the residue distilled. Di*iso*butylsulphone and di*iso*amylsulphone have b. p. 263° and 296° respectively (both with slight decomposition) (Beckmann, *J. pr. Chem.*, 1878, **17**, 448, gives b. p. 265° and 295° respectively.)

The effect of alkalinity upon the rate of oxidation of the sulphides was tested by means of eight solutions of sodium hypochlorite which contained 8·42% of available chlorine, but in which the alkalinity (calculated as sodium hydroxide) varied from 0·22% to 6·64%. Solutions of diethyl, di-*n*-propyl, di*iso*butyl, and di*iso*amyl sulphides were employed, having sulphur contents of, respectively, 0·736, 0·864, 0·912 and 0·875%. Preliminary experiments led us to adopt, for the times of shaking, 15, 30, 120, and 240 minutes, respectively. The results are summarised in Table I.

TABLE I.

Available chlorine in reagent = 8·42%.

Free alkali	Diethyl sulphide.		Di-*n*-propyl sulphide.		Di*iso*butyl sulphide.		Di*iso*amyl sulphide.	
%	*n*.	*x*.	*n*.	*x*.	*n*.	*x*.	*n*.	*x*.
0·22	4·08	Nil	4·17	0·04	3·81	0·58	3·94	0·86
0·37	4·26	,,	4·28	0·04	3·64	0·56	3·53	0·82
0·54	4·18	,,	4·27	—	3·37	0·78	2·68	0·81
0·91	4·24	,,	4·16	0·05	2·33	0·62	1·87	0·83
1·48	4·14	,,	3·91	0·09	1·68	0·56	1·28	0·78
2·87	4·15	,,	3·05	0·25	0·87	0·74	0·88	0·82
4·14	4·14	,,	2·00	0·43	0·62	0·86	0·74	0·84
6·64	4·02	,,	1·08	0·72	0·45	0·85	0·84	0·84

n = atoms of available chlorine absorbed, per atom of sulphur present.
x = % sulphur in residual petroleum.

Diethyl sulphide was always completely oxidised after 15 minutes; since diethylsulphone is much more soluble in water than in petroleum, the latter was invariably free from sulphur. It was, however, possible to demonstrate the retarding effect of sodium hydroxide on the oxidation of diethyl sulphide by using a solution of hypochlorite which contained 20·4% of sodium hydroxide and 7·89% of available chlorine; after 15 minutes, only 21·1% of the sulphide had been oxidised, and even after 60 minutes' shaking still only 53·4% had been removed. The inhibiting influence of the free alkali is more noticeable in the oxidation of the higher sulphides. Thus, with di-*n*-propyl sulphide there is a gradual diminution in the extent of oxidation, a correspondingly increasing quantity of sulphur remaining in the petroleum. In the case of di*iso*butyl and di*iso*amyl sulphides, the figures for the residual sulphur in the petroleum are irregular; this has been traced to the existence of a partition of the resulting sulphones between the aqueous reagent and the organic solvent. It was usual, before proceeding to the analysis of the petroleum layer, to wash it once or twice with a small quantity of sodium hydroxide solution to remove any free hypochlorous acid; in consequence, varying quantities of the higher sulphones were dissolved from the petroleum. This has been confirmed, for by washing petroleum solutions of di*iso*butyl- and di*iso*amyl-sulphones several times with water the sulphur content of the petroleum was reduced. Any of the sulphides dealt with was rapidly oxidised by a dilute, faintly alkaline, solution of sodium hypochlorite. It is evident that even using so strongly alkaline a solution as one containing 6·64% of free alkali, the reaction between aqueous sodium hypochlorite and a dialkyl sulphide may be said to proceed quite readily by comparison with the prolonged reactions which are so common in synthetic organic chemistry; and even with a reagent containing 20% of free alkali the reaction with diethyl sulphide is still obvious and could scarcely fail to be detected. In fact (*vide supra*), this reaction offers a very convenient method for the preparation of sulphones.

Organic Disulphides.

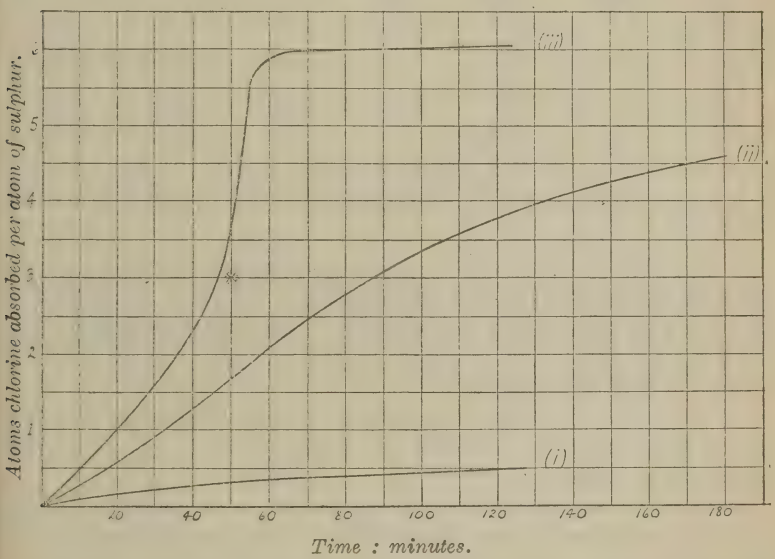
Diethyl and di*iso*propyl disulphides were quite readily freed from traces of the mercaptan or sulphide by fractional distillation. Their behaviour towards aqueous sodium hypochlorite is evidently typical of the disulphides, since parallel results were obtained in the two cases.

The primary oxidation products from diethyl disulphide, unlike the product from a sulphide, are acidic, *i.e.*, ethanesulphonic acid together with a smaller quantity of sulphuric acid; these appear as

sodium salts, and therefore the alkalinity of the aqueous phase is gradually reduced. Since the sulphonic acid (as its sodium salt) is not attacked by hypochlorite, the sulphuric acid is formed directly from the disulphide :

$$Na_2SO_4 \leftarrow H_2SO_4 \leftarrow R_2S_2 \rightarrow R{\cdot}SO_3H \rightarrow R{\cdot}SO_3Na.$$

The gradual removal of the alkali hydroxide makes it necessary, in describing the effect of alkalinity on the reaction, to distinguish two somewhat different cases. (1) The free alkali present is more than equivalent to the total possible acid products; the reagent will always remain alkaline. (2) The free alkali is less than equivalent



to the total possible acid products; if the reaction is continued long enough, the reagent will become acidic. The reaction in the first case may be described as the normal one; plotting the atoms of available chlorine absorbed, per atom of sulphur, against time, curves are obtained, of which (i), for a strongly alkaline, and (ii), for a weakly alkaline reagent, are typical. The influence of the added alkali hydroxide is very marked. If, however, the alkalinity of the reagent is so chosen that it falls into the second class, the additional complication causes the curve to assume quite a different form (iii). The initial part of the reaction takes the normal course until the acidic primary products have completely neutralised the free alkali present; at that point (*) there occurs a very rapid absorption of available chlorine until the sulphur compound is entirely removed

from the petroleum solution; the reaction then tails off and only a slow spontaneous decomposition of the residual dilute acid hypochlorite continues to take place.

TABLE II.

Diethyl disulphide. S = 0·63%. 25 C.c.

Time of shaking.	Sodium hypochlorite solution A (Cl = 5·43%; "NaOH" = 0·38%). 25 c.c.			Sodium hypochlorite solution B (Cl = 5·33%; "NaOH" = 0·73%). 25 c.c.		
Mins.	*d.*	*n.*	*x.*	*d.*	*n.*	*x.*
15	0·32	0·78	0·57	—	—	—
30	0·26	1·59	0·48	0·66	0·93	0·95
45	0·09	2·76	0·35	—	—	—
60	Nil	5·88	Nil	0·57	2·10	0·47
75	,,	5·90	,,	—	—	—
90	,,	5·91	,,	0·50	3·07	0·37
105	,,	5·98	,,	—	—	—
120	,,	6·15	,,	0·47	3·76	0·29
150	—	—	—	0·45	4·17	0·26
180	—	—	—	0·41	4·62	0·20

d = % "free alkali" in residual aqueous reagent. *n* = atoms of available chlorine absorbed per atom of sulphur present. *x* = % sulphur in residual petroleum.

A considerable evolution of heat occurred at and immediately after the point in the reaction marked with an asterisk; the oxidation at this stage was so rapid that a sample of the reagent corresponding with the points intermediate between this and the completion of the reaction could not be isolated.

It must be noted that even 20% of sodium hydroxide does not completely inhibit the oxidation of a disulphide by means of aqueous sodium hypochlorite.

Sodium ethanesulphonate was identified as a product of the oxidation of diethyl disulphide as follows. The disulphide, dissolved in petroleum, was shaken with a faintly alkaline solution of sodium hypochlorite in slight excess, until the mixture had become warm and had commenced to cool again. The aqueous liquid was warmed and treated with sulphur dioxide to decompose any residual hypochlorite and any sodium chlorate present. After adding an excess of hydrochloric acid, the excess of sulphur dioxide was expelled by boiling, and the solution neutralised, and evaporated to dryness. Sodium ethanesulphonate, mixed with sodium chloride, was extracted by means of absolute alcohol from the residue, dried at 110°. The pure salt was obtained after repeated crystallisation from absolute alcohol until it no longer contained chlorine (Found: Na, 17·4. Calc. Na, 17·5%).

A portion of the aqueous layer from the oxidation was boiled with ammonia, and hydrochloric acid and barium chloride were

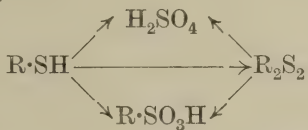
added; on boiling, a white precipitate of barium sulphate was obtained.

Mercaptans.

Ethyl mercaptan was used for these experiments; results obtained with *iso*propyl and *iso*butyl mercaptans indicated that the reactions followed the same course.

The mercaptans, before being fractionally redistilled, were washed with a small quantity of sodium hydroxide solution to remove any hydrogen sulphide.

The apparent course of the reaction between sodium hypochlorite and ethyl mercaptan depends greatly upon the alkalinity of the reagent. The first action leads simultaneously to the formation of ethanesulphonic acid, sulphuric acid, and diethyl disulphide; the last, if the reagent is sufficiently reactive, is destroyed as it is formed, the acids (as their sodium salts) being the only products. But with a more stable solution of hypochlorite a much slower decomposition of the disulphide occurs, and this substance then appears as the chief product, accompanied by smaller quantities of the acids, which have been formed, for the most part, by direct oxidation of the mercaptan. The first part of the reaction, in which the mercaptan itself takes part, does not appear to be affected by the alkalinity of the reagent, whilst the factors which influence the destruction of the resulting disulphide are those which govern the normal interaction of this type of compound with sodium hypochlorite (*vide supra*).



The proof that ethanesulphonic and sulphuric acids are formed concurrently with the disulphide is as follows: A solution of ethyl mercaptan containing 0·715% of sulphur and a solution of sodium hypochlorite containing 5·3% of available chlorine and 27·7% of sodium hydroxide being used, after 15 minutes 4·8 atoms of chlorine per atom of sulphur had been taken up, simple conversion to the disulphide requiring only one, and this figure did not appreciably increase after a further 45 minutes' agitation. This shows quite clearly that diethyl disulphide, once it is formed, is not appreciably attacked by hypochlorite having the alkalinity mentioned; this was confirmed by treating a solution of diethyl disulphide with the same reagent, when, even after 2 hours, only 0·4 atom of chlorine per atom of sulphur had been absorbed.

The influence of alkali hydroxide upon the extent of oxidation of

ethyl mercaptan during a fixed time of shaking is exhibited in Table III.

TABLE III.

Ethyl mercaptan solution : S = 0·715%.
Available chlorine = 8·42%. Time of shaking : 15 mins.

Free alkali %	0·22	0·37	0·54	0·91	1·48	2·86	4·14	6·64
Atoms Cl absorbed/ atom S	7·34	7·13	6·58	6·19	5·89	5·43	5·17	5·14
% S in residual petroleum	Nil	Nil	0·03	0·11	0·12	0·14	0·15	0·19

Ethanesulphonic acid was identified in the manner described above; the sodium salt was analysed (Found : Na, 17·4%). Sulphuric acid was identified as before. Diethyl disulphide was isolated from the petroleum at the conclusion of the reaction; the yield, however, never exceeded approximately 50%.

The Influence of Sodium Carbonate and the Effect of Dilution.

Solutions of sodium hypochlorite invariably contain sodium carbonate in addition to sodium hydroxide, sodium chloride, and sodium chlorate.

During the earlier experiments, estimations were made of the actual sodium hydroxide, as well as of sodium carbonate, in the aqueous reagent. The experimental procedure thereby involved made it, however, very inconvenient to carry out a sufficient number of experiments during many of the more rapid oxidations. In seeking a more simple method for determining the alkalinity of the hypochlorite, it was therefore necessary to ascertain whether sodium carbonate has any appreciable effect upon the reactivity of the reagent. For this purpose, the reaction with diethyl disulphide was chosen, as being the most sensitive towards the influence of added alkali. The results are summarised in Table IV, in which a comparison is drawn between the course of the reaction between a standard solution of diethyl disulphide and (i) a weakly alkaline solution of sodium hypochlorite, (ii) the same solution after the addition of solid sodium carbonate.

These figures do not show any detectable increase in stability brought about by the addition of sodium carbonate. This is scarcely surprising, since no appreciable alteration is produced in the concentration of hydroxyl ions by adding sodium carbonate to a solution already containing a comparatively large quantity of sodium hydroxide.

It was, in consequence, possible to adopt quite a simple method for determining the alkalinities of a series of reagents. The object of these analyses was twofold; the decrease in the alkali present before and after a reaction gave a measure of the acid products,

Table IV.

Diethyl disulphide solution : S = 0·631%. 25 C.c. taken.

Time of shaking.	Sodium hypochlorite solution "A" (Cl = 5·43%; "NaOH" = 0·38%). 25 c.c.			Solution "A" plus solid sodium carbonate (Cl = 5·33%; "NaOH" = 0·38%; *Na_2CO_3 = 0·37%).			
Mins.	*d.*	*n.*	*x.*	*d.*	*n.*	*x.*	*β.*
15	0·32	0·78	0·57	0·71	0·67	0·57	2·59
30	0·26	1·59	0·48	0·64	1·49	0·51	3·24
45	0·09	2·76	0·35	0·59	2·20	0·42	7·09
60	Nil	5·88	Nil	—	—	—	—
75	,,	5·90	,,	0·20	5·71	Nil	6·88
90	,,	5·91	,,	0·20	5·73	,,	6·62
105	,,	5·98	,,	—	—	—	—
120	,,	6·15	,,	—	—	—	—

Time of shaking.	Solution "A." 25 c.c., plus 25 c.c. of water.			Solution "A." 25 c.c., plus 100 c.c. of water.		
Mins.	*d.*	*n.*	*x.*	*d.*	*n.*	*x.*
15	0·13	2·95	0·35	Nil	5·45	0·02
30	Nil	5·78	Nil	,,	5·53	Nil
45	,,	5·80	,,	—	—	—
60	,,	5·88	,,	—	—	—
75	,,	5·90	,,	—	—	—

d = % "free alkali" in residual aqueous reagent.
n = atoms of available chlorine absorbed per atom of sulphur present.
x = % sulphur in residual petroleum.
β = % of total sulphur which appears as sulphuric acid.

* Calculated as sodium hydroxide.

whilst the alkalinities of a series of reagents formed an indication of their reactivities. The solutions all contained approximately the same concentration of sodium carbonate, present as impurity in the weakly alkaline solution of sodium hypochlorite to which varying quantities of solid sodium hydroxide had been added. Since differences in alkalinity were to be compared, as distinct from the actual hydroxyl-ion concentrations, the alkalinity was estimated, after destroying the hypochlorite by means of hydrogen peroxide, by titration against hydrochloric acid with methyl-orange as indicator. Hence curves in which alkalinity is plotted as one of the co-ordinates are slightly displaced in a direction parallel to the axis of alkalinity; for the present purpose this is immaterial.

The increase in reactivity brought about by diluting a solution of sodium hypochlorite (compare p. 1936) was demonstrated by means of the reaction with diethyl disulphide. The reagent used was the same solution which had been employed for the experiments with sodium carbonate; in one series the solution was diluted to one-half, in the second to one-fifth of its original concentration. The results, which clearly indicate an increase in the velocity of reaction with

decrease in concentration of the sodium hypochlorite, are included in Table IV.

Elementary Sulphur and Hydrogen Sulphides; Thiophen.

The observation of Wood, Lowy, and Faragher (*loc. cit.*) that free sulphur is precipitated when hydrogen sulphide reacts with sodium hypochlorite, has been confirmed, but evidence of the simultaneous production of sulphuric acid has been obtained. This is not formed by further oxidation of the elementary sulphur, since the latter has been shown to be quite inert towards sodium hypochlorite.

Thiophen does not react with sodium hypochlorite.

Our thanks are due to Professor J. F. Thorpe, C.B.E., F.R.S., for his kind help and encouragement and to Dr. A. E. Dunstan and Dr. F. B. Thole for their interest in the present work.

ANGLO-PERSIAN OIL CO., LTD.,
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CCLX.—*The Action of Formic Acid on certain Sesquiterpenes.*

By JOHN MONTEATH ROBERTSON, CARL ALOYSIUS KERR, and GEORGE GERALD HENDERSON.

THE experiments described below were undertaken last year as part of a larger investigation which is not yet complete, but it appears desirable to communicate the results now, in view of the interesting work carried out recently by Ruzicka and Capato (*Helv. Chim. Acta*, 1925, **8**, 259).

The action of anhydrous formic acid as a means of effecting ring closure in the sesquiterpenes is now well established. Semmler and Spornitz (*Ber.*, 1913, **46**, 4025) ascertained the transition of the aliphatic sesquiterpene from Java-citronella oil into a monocyclic isomeride by the action of concentrated formic acid. Ruzicka and Capato (*loc. cit.*) in their synthesis of bisabolene from nerolidol have now shown that the action of formic acid in the cold closes one ring in the nerolidol structure, whereas, by more prolonged action with the same reagent at a higher temperature, the closure of two rings is effected, a hexahydrocadalene being thus produced. They also observed the production of alcohols as intermediate compounds.

This reagent may also act in another way, as was shown by Wallach (*Annalen*, 1896, **289**, 337), who found that on refluxing

pulegone with anhydrous formic acid for several days, acetone and 1-methyl-3-*cyclo*hexanone resulted.

We have investigated the action of anhydrous formic acid on the dicyclic sesquiterpenes β-caryophyllene and cadinene and on the tricyclic sesquiterpene cedrene, and our results support the above conclusions with regard to the efficacy of this reagent in producing isomeric hydrocarbons and in effecting ring closure.

From β-caryophyllene we obtained the *formic* ester, $C_{16}H_{26}O_2$, of caryophyllene alcohol, together with a mixture of hydrocarbons, probably consisting of clovene and unattacked caryophyllene. Since caryophyllene alcohol is a saturated substance and on dehydration yields clovene, it is presumably tricyclic. Hence in this case the action of formic acid has effected ring closure, the sesquiterpene passing from the dicyclic caryophyllene structure to the tricyclic clovene structure.

The chief product from cadinene consisted of a hydrocarbon, or a mixture of hydrocarbons, $C_{15}H_{24}$, b. p. 118—124°/9 mm., which did not form a stable hydrochloride, together with some unchanged cadinene. On heating cadinene in an autoclave, Semmler and Jakubowicz (*Ber.*, 1914, **47**, 2252) obtained a substance, b. p. 120—130°, d 0·9025, n_D 1·50829, which they considered to be a monocyclic sesquiterpene mixed with cadinene. The product we obtained agrees closely with the above in its physical properties.

Cedrene yielded as chief product an isomeric unsaturated hydrocarbon, b. p. 114—118°/9 mm., some unchanged cedrene, and a small fraction of higher boiling point in which the presence of alcoholic compounds is suspected.

Experimental

Action of Formic Acid on β-Caryophyllene.—β-Caryophyllene was prepared by fractional distillation under diminished pressure of the commercial hydrocarbon which had stood for some time in contact with solid potassium hydroxide. The main product had b. p. 118—119°/9·7 mm., $n_D^{17°}$ 1·5009, $d_4^{17°}$ 0·9052, and gave a practically quantitative yield of the crystalline dihydrochloride of β-caryophyllene, m. p. 69°; $[\alpha]_D^{15°}$ + 67·2° in 2·5% ethyl-alcoholic solution. Caryophyllene (25 c.c.) was heated under reflux with an equal amount of formic acid for several days. A reaction set in at once, and when completed the excess of acid was neutralised with sodium carbonate, and by extraction of the mixture with ether an oil was obtained which after several fractionations yielded a colourless liquid, b. p. 141—145°/10 mm., $d_4^{17°}$ 1·22, $n_D^{20°}$ 1·4967, $[\alpha]_{5461}^{17°}$ − 10·46°. Analysis indicated that this liquid was the formic ester of caryophyllene alcohol, $C_{15}H_{25}O(CHO)$ (Found: C, 76·9; H, 10·5.

$C_{16}H_{26}O_2$ requires C, 76·8; H, 10·4%), and this was confirmed by hydrolysis of the ester, when the alcohol was obtained in crystals, which, after recrystallisation from ether–light petroleum, melted at 96°. The yield of the ester was about 35% of the caryophyllene taken. The other fractions of the distillation, b. p. 115—130°/10 mm., consisted of hydrocarbons. Heating caryophyllene in a sealed tube at 200° with anhydrous formic acid for 5 hours did not lead to an increased yield of the formic ester.

Action of Formic Acid on Cadinene.—Cadinene was prepared from the dihydrochloride, m. p. 118°, by regeneration with anhydrous sodium acetate in glacial acetic acid solution. Equal quantities of cadinene, b. p. 134—136°/11 mm., $d_4^{20°}$ 0·9189, $n_D^{20°}$ 1·5079, $[\alpha]_{5461}^{18°}$ − 125°, and 99% formic acid were heated together under reflux at 100° for 40 hours. The liquid slowly became red. After neutralisation, the products were extracted with ether and hydrolysed. The final products were distilled under diminished pressure. After several distillations two main fractions were obtained: (*a*) b. p. 118—124°/9 mm. and (*b*) b. p. 126—134°/9 mm., together with some brown resinous substances. The fraction (*a*) consisted of an unsaturated hydrocarbon, $d_4^{17°}$ 0·9086, $n_D^{14°}$ 1·5010 (Found: C, 87·3; H, 12·1. $C_{15}H_{24}$ requires C, 88·2; H, 11·85%). The fraction (*b*) consisted chiefly of unchanged cadinene.

Action of Formic Acid on Cedrene.—Cedrene, purified by distillation over sodium, b. p. 122—124°/9 mm., $d_4^{20°}$ 0·9361, $n_D^{21°}$ 1·5005, was treated with formic acid in the same way as cadinene, and the products were worked up as before. After a large number of distillations under reduced pressure, the following fractions were obtained: (*a*) b. p. 114—118°/9 mm., comprising about 50% of the product; (*b*) 118—130°/9 mm.; (*c*) 130—135°/9 mm., a small fraction. The fraction (*a*) consisted of an unsaturated hydrocarbon, $d_4^{20°}$ 0·9333, $n_D^{21°}$ 1·4988 (Found: C, 87·9; H, 11·9. $C_{15}H_{24}$ requires C, 88·2; H, 11·8%), from which no derivative could be obtained. It appears to be tricylic from its physical constants. The fraction (*b*) consisted chiefly of unattacked cedrene The fraction (*c*) appears from its analysis to contain alcoholic substances as well as hydrocarbons (Found: C, 84·8; H, 11·25%), but only a small quantity was available.

We are indebted to the Carnegie Trust for grants which enabled us to carry out this work.

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CCLXI.—*Cryoscopic Measurements with Benzene.*

By Edward Richard Jones and Charles R. Bury.

The object of the work described in this paper was to see how far certain conclusions, reached in the study of nitrobenzene as a solvent for cryoscopy, could be applied to benzene, a far more important solvent from the point of view of ordinary laboratory practice.

First, the most important source of error is the change in water content of the solvent: this is usually overlooked with benzene, but is by no means negligible in accurate work (Sidgwick, J., 1920, **117**, 1340). The difference between the freezing point of dry and of wet benzene is 0·097° (Sidgwick, *loc. cit.*; Richards, Carver, and Schumb, *J. Amer. Chem. Soc.*, 1919, **41**, 2024). This error can be easily avoided by keeping the solvent in contact with a substance the aqueous vapour pressure of which is constant (Roberts and Bury, J., 1923, **123**, 2037).

Secondly, the usual van 't Hoff formula is strictly true only at infinite dilution; with depressions up to about 0·5° the error due to the use of this formula is less than the experimental error. At greater concentrations, however, far more accurate results may be obtained from the formula discussed by Brown and Bury (J., 1924, **125**, 2219):

$$\Delta t_u + \Delta t_w = k[n_u + Cn_v]/[n_u + (1 + C)n_v],$$

where Δt_u is the observed depression, n_u and n_v are the number of mols. of solute and solvent respectively, Δt_w and C are constants depending on the degree of moisture of the solvent, *i.e.*, on the vapour pressure of the substance with which it is in contact. These have been calculated by the method described by Brown and Bury, assuming that the freezing point of benzene is a linear function of the aqueous vapour pressure (Crowther and Puri, *Proc. Roy. Soc.*, 1924, *A.*, **106**, 232). For the substances used in this research the values are:

	Aq. vap. pressure.	Δt_w.	C.
Phosphorus pentoxide, alumina ...	0·0 mm.	0	0
$Na_2SO_4,0—10H_2O$	4·40	0·063°	0·00094
Water	6·76	0·097	0·00145

With this formula it should be possible to detect combination between solute and solvent, or solvation (Washburn, " Principles of Physical Chemistry," 1915, p. 174). If every molecule of solute combines with N of solvent, the number of mols. of solute is unaltered, but the number of mols. of solvent is reduced by Nn_u: when N is 1, and the solvent is dry, the formula given reduces to that of van 't Hoff. Azobenzene, triphenylmethane, picric acid,

and trinitrotoluene, all of which separate from benzene with 1 mol. of benzene of crystallisation, have been studied to see if solvation can be detected. The existence of solid compounds is, of course, no proof that these substances form compounds with benzene in solution. It is, however, probable that the compounds of picric acid and trinitrotoluene with benzene exist in solution, since similar compounds, such as naphthalene picrate, are not entirely dissociated in inert solvents (Brown, this vol., p. 345).

Experimental.

The benzene used was a pure thiophen-free sample supplied by Robinson, Nelson and Co., and was further purified by the method described by Roberts and Bury (*loc. cit.*). The substances used as solutes were chosen with the idea of covering as wide a range of types of compounds as possible, and were all purified by repeated crystallisation.

The usual Beckmann method was employed. All depressions recorded are the mean of at least three closely agreeing determinations. After a number of preliminary experiments, it was decided that the loss of solvent by evaporation could not be avoided without seriously complicating the apparatus, but was negligible provided the experiment did not last more than $2\frac{1}{2}$ hours.

The degree of supercooling attainable varies rather remarkably with conditions : with very pure and dry benzene it is difficult to get that small amount of supercooling which is essential to the Beckmann method; with the wet solvent, however, it is difficult to avoid a supercooling of 2°.

The freezing point of benzene has been found to be much more susceptible than that of nitrobenzene to errors due to friction and radiation, depending on the rates of stirring and the temperature of the bath. These were minimised as far as possible by maintaining a standard rate of stirring and by keeping the bath temperature 1—1·5° below the freezing point. In working with the dry solvent in the presence of phosphorus pentoxide, the usual precaution of passing dry air through the apparatus could not be used on account of the volatility of the solvent; consequently the phosphorus pentoxide soon became sticky, and the frictional effects generated by stirring made the determination of the freezing points difficult. Alumina was found to be nearly as efficient as a drying agent, and free from this disadvantage.

Conclusions.

A typical selection of the results obtained with normal solutes is given in Table I; the first column gives the weight of solute per

100 g. of solvent (W), the second the observed depression, and the third the molecular weights (M) calculated from the above formula. The solute, its molecular weight, and the degree of moisture of the solvent are given at the head. (Na_2SO_4 signifies that the solvent was partially saturated, in contact with the salt hydrate pair Na_2SO_4,0—10H_2O.) It is obvious that the calculated molecular weights are more consistent and accurate than are obtained by the usual Beckmann method, *i.e.*, by using the van 't Hoff formula, and neglecting the changing water content of the solvent.

TABLE I.

Naphthalene (128·1), dry (P_2O_5).			*p*-Dibromobenzene (235·9), dry (Al_2O_3).		
W. (g.).	Δt_u.	M.	W (g.).	Δt_u.	M.
2·504	1·005°	128·3	5·147	1·119°	236·4
3·204	1·283	128·1	9·933	2·130	236·0
5·009	1·984	128·1	11·811	2·519	235·9
5·935	2·338	128·1	13·963	2·949	236·6
6·345	2·491	128·2	16·573	3·479	236·1
7·706	3·001	128·2	19·473	4·060	235·5
10·725	4·112	128·0	21·965	4·547	235·4
Naphthalene, Na_2SO_4.			*p*-Dibromobenzene, Na_2SO_4.		
1·855	0·745	128·4	5·645	1·223	236·5
3·802	1·515	128·0	8·309	1·790	235·7
7·510	2·930	127·9	9·682	2·073	236·1
9·150	3·529	128·1	12·317	2·621	235·6
12·117	4·603	127·9	14·977	3·158	235·7
Naphthalene, saturated.			Camphor (152·2), Na_2SO_4.		
1·911	0·770	127·9	2·901	0·984	151·6
3·106	1·243	127·8	4·488	1·505	152·1
6·324	2·476	128·1	5·733	1·912	152·0
9·028	3·486	127·9	8·641	2·834	152·3
11·701	4·451	127·9	10·605	3·461	151·6
Anisole (108·1), Na_2SO_4.			Azobenzene (182·2), Na_2SO_4.		
2·515	1·192	108·1	3·806	1·071	182·5
4·060	1·907	107·9	5·702	1·594	182·2
7·976	3·649	107·8	6·865	1·907	182·5
9·171	4·161	107·9	8·432	2·331	182·2
10·257	4·629	107·6	10·473	2·866	182·5

The results obtained with the dry solvent, and quoted in this table, were used to calculate k. Assuming the theoretical molecular weights, the mean value found was 66·95, and this has been used in calculating the figures in the third column. This value corresponds to a value of 52·27 for the van 't Hoff constant, and 29·53 cals. for the latent heat of fusion of benzene. The published values for the latent heat are somewhat conflicting, and vary from 29·1 to 30·7 cals. : most direct determinations of the van 't Hoff constant are rather lower than 52·27, but it must be remembered that low values for this constant must always be obtained when working with solutions that are not infinitely dilute (Brown and Bury, *loc. cit.*).

With benzene, in which water is only very slightly soluble, little error is introduced by neglecting the water content of the solvent in calculating molecular weights, provided, of course, that it is kept constant during the experiments. If C and Δt_w are put equal to 0, as when working with the dry solvents, the calculation is considerably simplified, and the error introduced is only about 0·2%.

We have obtained no definite evidence of solvation. Azobenzene (Table I) is a perfectly normal solute. With picric acid and trinitrotoluene, the deviation that might be expected if solvation occurs is masked by a deviation in the opposite direction, possibly due to association. Triphenylmethane appears to be solvated but is, unfortunately, too insoluble for the evidence to be conclusive. The maximum depression obtainable is rather less than 0·8°, and such small depressions are liable to an experimental error of 0·5%, which is comparable with the theoretical deviation (1%) to be expected if solvation occurs. Values of k and of the van 't Hoff constant K, calculated from the experimental results with triphenylmethane, are shown in Table II. The van 't Hoff law appears to fit the

TABLE II.

Triphenylmethane (242·2), Na_2SO_4.

W. (g.).	Δt_u.	k.	K.
2·434	0·521°	67·53	52·27
2·567	0·550	67·63	52·33
2·617	0·560	67·56	52·26
2·934	0·627	67·54	52·19
3·212	0·689	67·84	52·39
3·356	0·718	67·71	52·26
3·526	0·755	67·78	52·29
	Mean	67·66	52·28
	Theory	66·95	52·27

TABLE III.

Tetrachloroethane (167·9), dry (Al_2O_3).

W. (g.).	Δt_u.	M.	k.
2·888	0·888°	167·7	67·01
4·314	1·315	168·1	66·87
5·561	1·692	167·5	67·12
8·117	2·450	166·9	67·36
12·587	3·769	164·7	68·16
14·691	4·380	163·9	68·49
17·304	5·147	162·2	69·11

results better, which indicates solvation, for the mean value of K is nearer than that of k to the values of these constants obtained with normal substances; k shows a distinct tendency to increase with the concentration whilst the variation of K is haphazard.

Substances tend to be more abnormal in benzene than in nitrobenzene. No solute which has been found normal in benzene, and which has also been studied in nitrobenzene, has proved to be abnormal in the latter solvent, but many solutes, normal in nitrobenzene, are abnormal in benzene, *e.g.*, picric acid, trinitrotoluene, methyl oxalate, α-nitronaphthalene, tetrachloroethane, and benzil. In the majority of cases these substances appear to be associated and we hope to discuss this phenomenon fully in a later paper. Tetrachloroethane behaves in a somewhat unusual manner: it is normal in dilute solution, but the law for normal substances

breaks down at higher concentrations: as shown in Table III, the calculated molecular weights are too small at the higher concentrations.

One of us (E. R. J.) desires to acknowledge his indebtedness for a Garrod Thomas research scholarship of this College.

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CCLXII.—*The Condensed Ternary System Phenol–Water–Salicylic Acid.*

By CHARLES REYNOLDS BAILEY.

TERNARY systems containing water and two organic substances have attracted workers on phase rule questions because of the varied phenomena which are to be met with. In one or more of the binary systems concerned, an upper or lower critical solution temperature frequently occurs and two liquid layers are to be found; references to many systems will be seen in Vols. II, ii, and III, ii, of Roozeboom's "Die Heterogenen Gleichgewichte" and in Tammann's work on the same subject. Difficulties in the quantitative analysis of such systems where mixtures of organic substances are involved have generally led to the restriction of their examination to the "synthetic" method; this method neglects the possible formation of mixed crystals; in the present research both analytic and synthetic methods have been applied.

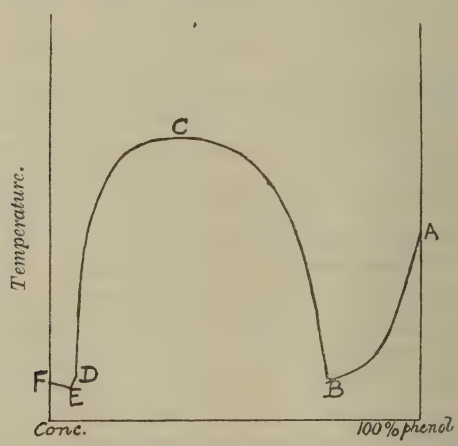
The system phenol–water–salicylic acid was chosen as it presents certain features of considerable interest and it was anticipated that by the interplay of these characteristics important solubility relations would arise. Some of the chief points are: (i) the binary system water–salicylic acid gives two liquid layers in the metastable region; (ii) the system phenol–water has two liquid layers in the stable region and the phenomenon of "melting under the liquid" occurs at an easily accessible temperature; (iii) salicylic acid has very slight solubility in water but a much higher solubility in phenol.

By use of the synthetic method it has been possible to extend the research well into the metastable region. In applying the analytic method the mixtures were stirred in a thermostat, the one or two liquid layers sucked off and, together with the moist residue, analysed as indicated below.

The Binary Systems.

(1) *Phenol–Water.*—Temperature–concentration diagrams have been given by Smits and Maarse (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 192) and by Rhodes and Markley (*J. Physical Chem.*, 1921, **25**, 527). The former workers do not give the concentrations which correspond to many of the phase changes, although the temperatures are in general agreement with those obtained by the latter workers. No trace of the stable phenol hydrate was observed in the present research and the values for certain binary and ternary mixtures are strictly metastable. The two-liquid-layer area has been explored by a large number of workers and no two determinations seem to agree, the departure from the mean being

FIG. 1.



greatest at high temperatures. In many cases this is due to the use of impure materials and in others to inaccurate use of the synthetic method. Most workers have taken as the critical saturation temperature the mean between the temperatures of clouding and clearing. If, however, the very definite temperature of sudden thickening is taken, it is possible to get readings concordant to 0·1° and agreeing with those of Timmermans (*Z. physikal. Chem.*, 1907, **58**, 129) and with the values obtained by analysis of the two liquid layers after the mixture has completely cleared in a thermostat. The difficulty does not occur to the same marked extent at lower temperatures, and it is possible to correct the concentration given by Rhodes and Markley (*loc. cit.*) for the point D (Fig. 1) where solid phenol is in equilibrium with a water-rich solution. The concentration given is 10·0% phenol at 1·7°, which is well inside the two-liquid layer area: the true concentration at this

point is 7·6% and agrees with a redetermination made by the present author by thermal analysis.

The important temperatures in the system are as follows, the letters referring to Fig. 1 :—

TABLE I.

Point.	% Phenol.	Temp.	
A	100·0	40·8°	M. p. of pure phenol
B	75·0	1·7	
C	36·5	65·3	Crit. soln. temp.
D	7·6	1·7	
E	6·5	−1·2	Eutectic
F	0·0	0·0	M. p. of ice

(2) *Salicylic Acid–Water.*—Here again many incomplete determinations are to be found in the literature; the values for the solubility of salicylic acid in water are extremely divergent: the most recent data, due to Savorro (*Atti R. Accad. Sci. Torino*, 1914, **48**, 948) are not only above the mean of the best data available, but exhibit several breaks in the curve which do not correspond to any accompanying phase change. The values obtained in the present research (Table II) coincide with those of Walker and Wood (J., 1898, **73**, 620) up to 30°, but are slightly and uniformly larger at higher temperatures. A fresh determination of the metastable region has been made and the results differ slightly from those of Flaschner and Rankin (*Monatsh.*, 1910, **31**, 23). A careful determination of the eutectic ice–salicylic acid places this at − 0·07° and 0·103% salicylic acid.

TABLE II.

(The values are given in grams per 100 g. of solution.)

Stable.		Metastable.		
		Water layer.	Salicylic layer.	
% Sal.	Temp.			Temp.
0·131	10·0°	4·4	69·6	60·0°
0·184	20·0	6·5	64·6	70·0
0·261	30·0	9·8	55·9	80·0
0·395	40·0	15·0	46·0	85·0
0·592	50·0	30·0	30·0	87·0
0·864	60·0			

(3) *Phenol–Salicylic Acid.*—This system does not appear to have been previously investigated. Walden (*Z. physikal. Chem.*, 1920, **94**, 331) found that the depression of freezing point of phenol by salicylic acid was normal. In the present case thermal analysis was resorted to; at the higher temperatures near the melting point of the acid, mixtures were sealed in glass tubes, and the temperatures of appearance and disappearance of the solid phase noted. At the lower temperatures the eutectic halts were measured

and it was found that their prolongation met the composition axis at 100% salicylic acid. Hence the system offers a simple eutectic at 5·0% salicylic acid and 38·16°. The results are given in Table III. For the mixture containing 1·5% acid the lowering of the phenol freezing point is 0·8°; if the cryoscopic constant for phenol is taken as 72·7, the molecular weight of the acid is 138·7 (calc. 138·1).

TABLE III.

No.	Wt. % of salicylic acid.	Temp.	Temp. of eutectic.	Duration of halt in minutes.
1	0·0	40·80°	—	—
2	1·64	39·95	—	—
3	3·17	39·12	38·10°	18
4	4·39	38·47	38·16	25
5	5·00	38·16	38·16	28·5
6	7·38	45·9	38·18	28
7	10·09	55·6	38·07	27·5
8	14·2	65·6	37·9	26
9	27·5	89·2	38·0	23
10	46·0	113·5	—	—
11	60·0	128·7	38·0	—
12	81·8	147·2	—	—
13	94·9	157·0	—	—
14	100·0	160·4	—	—

EXPERIMENTAL.

Materials.—(i) *Phenol.* The detached crystals marketed by the British Drug Houses seem to be a very satisfactory product, and preserve their whiteness unchanged even on long exposure to light. They were twice distilled and the end portions rejected in each case; the product obtained melted at 40·8°.

(ii) *Salicylic acid.* Both the commercial variety and the physiologically pure acid were used. The samples were recrystallised by dissolving in boiling water and pouring into cold: the process was carried out four times. This removes completely the sweet smell characterising the commercial acid, which is nevertheless of a high degree of purity nowadays. The brown colour found in specimens of the physiologically pure acid is not removed in this way. The older methods for effecting this involved distillation in steam or solution in glycerol, whereas it was found best to dissolve the acid in a hot mixture of phenol and water; on cooling, the colourless acid was precipitated and a further supply was obtained by adding water to the mixture. If the solution of the acid in hot water is allowed to cool slowly, the peculiar formation of crystalline threads may be observed (*Nature*, 1923, **112**, 10). After the last two crystallisations the m. p. was constant at 158·7°; when allowance is made for stem exposure, this figure is increased to 160·4°, a result much higher than is usually found in the literature but

agreeing with that of W. J. Bush and Co., Ltd. (*Perfumery and Essent. Oil Rec.*, 1920, **11**, 207). The value was checked by observations both on a single crystal in a melting point tube and also by cooling curves on a large bulk of the acid.

Analysis of Solutions.—Phenol was estimated by the bromide–bromate method (for details, see Redman, Weith, and Brock, *Ind. Eng. Chem.*, 1913, **5**, 389).

Salicylic acid can be directly estimated with baryta; the indicator chosen was *p*-nitrophenol with titration to a colour match. Kolthoff (*Pharm. Weekblad*, 1921, **58**, 699) has examined the bromometric method in use for phenol as applied to salicylic acid; by careful standardisation of conditions he obtained concordant results. The present author finds that with reasonable care reproducible results are obtained for one and the same concentration of acid, but if that concentration is varied the titre value does not change proportionally. Curves correlating concentration and bromide–bromate titre were constructed but found too complicated to be of use.

Phenol and salicylic acid in mixture in aqueous solution were analysed by various methods, of which the most successful were the following:

(i) By separation and subsequent determination: the phenol was extracted several times with small quantities of ether or chloroform from a solution containing a slight excess of sodium bicarbonate and the extracts were added to caustic soda solution. It was found necessary to drive off all traces of the organic solvent before bromination, as, peculiarly enough, much less bromine was taken up in its presence.

(ii) The method finally adopted was to determine first the salicylic acid alone; this can be effected by titration with baryta and *p*-nitrophenol indicator, since by keeping the phenol in low concentration it has no effect on the indicator. It was then ascertained by careful varying of the concentrations that the presence of the one substance does not affect the bromination of the other in mixtures of phenol and salicylic acid. The total bromide–bromate titre was accordingly determined for a given volume of the solution and the *same* volume of the solution was then evaporated to dryness with excess of sodium bicarbonate solution; this treatment was shown to be sufficient to drive off the phenol and leave the acid as the sodium salt, which was then brominated. The difference between the two titres gives the phenol in the mixture, since it has been shown above that with the same concentration of salicylic acid reproducible results can be obtained on bromination.

Water was determined by difference.

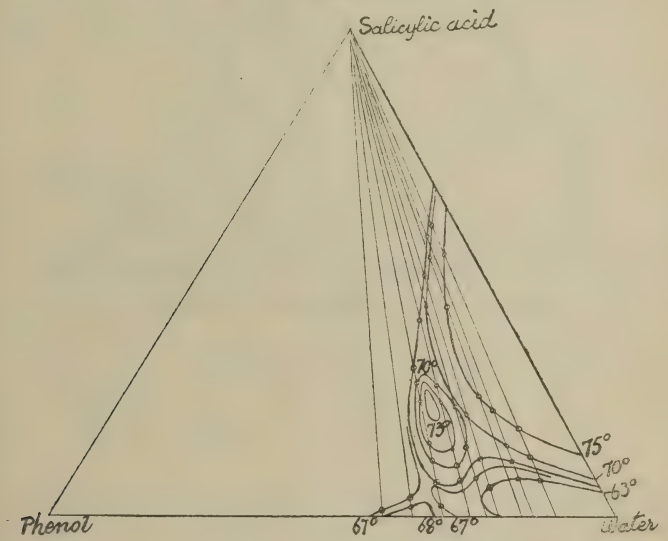
The mixtures were stirred in a thermostat for temperatures

between 20° and 70°. When equilibrium (which was approached from both sides) had been attained, the solution was sucked off through a side tube with filter into a stoppered flask and weighed, transferred to a measuring flask, and made up to a known volume. The conjugate solutions in the case of two liquid layers were allowed to settle out from the emulsion formed and sucked off; fortunately at the higher temperatures the clearing was only the matter of an hour or so; at the lower temperatures a longer period of standing was necessary. The moist residues were analysed similarly to give the solid phase.

The ternary system was also explored by the synthetic method for control purposes and to investigate the metastable region. Varying amounts of salicylic acid were added to known mixtures of phenol and water and the temperature of sudden thickening was determined; separate determinations agreed to within 0·1°. The work was carried out in sealed tubes. At the same time the temperature of the beginning of critical opalescence was determined; it was found possible to obtain reproducible readings within 0·5°. Curves were then constructed showing the relation between the above temperatures and the concentrations of salicylic acid in the particular mixture; from a given series of curves the percentages of salicylic acid present at constant temperature can be laid off: then on the usual triangular diagram the points on the phenol–water axis representing the different initial mixtures taken can be joined to the salicylic acid vertex; the percentages of acid obtained from the previous curves can be marked directly on to the triangular diagram and hence the isotherms are obtained (Figs. 2 and 3). It was found possible to complete the larger number of isotherms having metastable prolongations and so to explain the rather peculiar shape of the binodal curves. In this way two distinct series of isotherms are got and it is interesting to contrast one with the other (Figs. 2 and 3). Both temperatures from their reproducibility seem to be characteristic of the particular mixture under consideration, but it is difficult to trace any relationship between them; there are cases in which the addition of further quantities of the third component lowers the temperature of sudden thickening but actually raises the temperature of beginning of opalescence. There is apparently a " knoll " on the contour system for the critical opalescence which finds no corresponding feature on the system as determined by analysis or by the sudden thickening (the last two methods giving concordant results). Andant (*J. Phys. Radium*, 1924, **5**, 193), in an examination of the opalescence of a liquid and its vapour at the critical temperature, was able to show that the intensity and duration of the opalescence

varied with the ratio of the volume of liquid to that of vapour, passing through a maximum when the ratio was unity. In the case of binary and ternary mixtures where the upper liquid layer bears some rough analogy to the vapour phase in the unary equilibria, the correspondence would predict a condition of maximum opalescence for mixtures which are in the neighbourhood of the critical point on the particular binodal curve under consideration. This is roughly borne out by the experimental results, as will be seen on reference to Table V; in mixtures containing a large proportion of any one constituent, and hence generally resolving into

FIG. 2.



Critical opalescence isotherms.

two liquid layers with a large volume ratio, the temperatures of critical opalescence and critical thickening coincide almost exactly.

At temperatures below 20°, the system was examined by thermal analysis in a vacuum vessel; the curve which gives the displacement of the temperature at which solid phenol can exist in contact with two liquid layers on addition of the third component was obtained in that way.

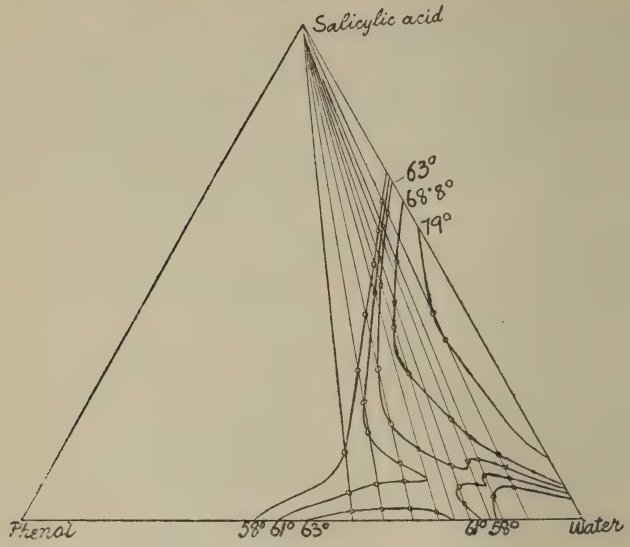
No compounds or mixed crystals were observed during the investigation.

The Isotherms.

A selection of the tabulated results will be found at the end of the paper. The two series of isotherms illustrated in Figs. 2 and 3

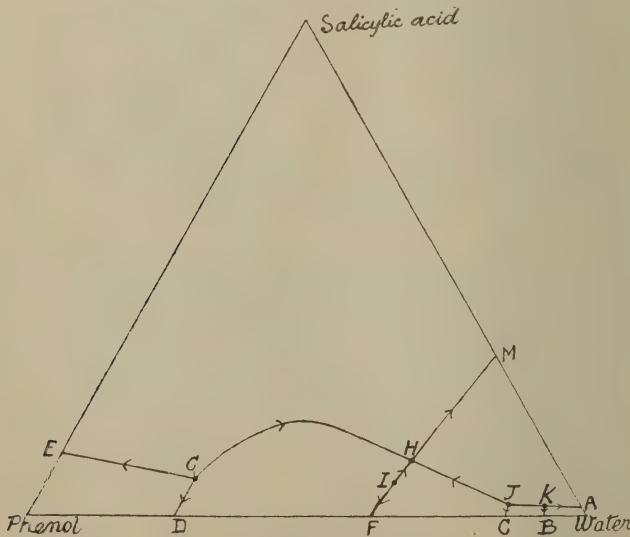
contain only the binodal curves; the inclusion of the saturation curves for solid salicylic acid would have complicated them unduly.

FIG. 3.



Binodal curves as determined by analysis.

FIG. 4.



It is expedient to consider, first, the polytherm for the system, and, secondly, the individual isotherms in order to obtain a grasp

of the many phase changes which may take place within narrow temperature limits.

The Polytherm (Fig. 4).—The actual conditions in the bottom right hand corner of the diagram have been exaggerated somewhat in order to render them apparent; the necessity for this will be readily seen on consideration of the values given below (Table IV). The arrows indicate the direction of rising temperature. To indicate the phases present the following symbols will be adopted: Solid salicylic acid S; solid phenol P; ice W; and where two coexistent liquid phases are possible: (low acid content) layer rich in phenol L_1, layer rich in water L_2; (low phenol content) layer rich in acid L_3, layer rich in water L_4. Metastable results throughout are enclosed in square brackets.

TABLE IV.

		Temp.	Percentage by weight. Phenol.	Acid.	Water.
Binary equilibria :—					
A.	S + W	−0·07°	—	0·103	99·9
B.	P + W Eutectics	−1·20	6·5	—	93·5
E.	S + W	38·16	95·0	5·0	—
C.	P + L_2 P. in equil. with	1·7	7·6	—	92·4
D.	P + L_1 two liq. layers .	1·7	75·0	—	25·0
F.	L_1 + L_2 Critical points	65·3	36·5	—	63·5
M.	[L_3 + L_4]	[87·0	—	30·0	70·0]
Ternary equilibria :—					
K.	S + P + W Eutectic ...	−1·3	6·5	0·2	93·3
I.	(See below)	61·2	20·4	7·6	72·0
H.	L_3 + L_4 + S.....	63·4	21·7	12·7	65·6
G.	S + P + L_2 Two liquid	−0·6	6·6	0·2	93·2
J.	S + P + L_1 layers, S and P.	−0·6	69·9	4·2	25·9

According to Schreinemakers's generalisation (*Z. physikal. Chem.*, 1898, **25**, 320) the temperature of melting under the liquid is depressed by the addition of a third substance when that substance is more soluble in the liquid layer which is rich in the "melting constituent." This is again confirmed: solid phenol is in equilibrium with two liquid layers at D and C; on addition of the acid the temperature and concentration of the ternary univariant phenomenon shift from B → G and C → J (from 1·7° to − 0·6°). The points K (the ternary eutectic) and J are so near to each other that the equilibria J → K are practically unrealisable. K, G, and J are system invariant points, since four phases and vapour are in equilibrium at constant pressure. F → I shows the progress of the phenol–water critical point on the addition of salicylic acid; the latter is soluble to some extent in both liquids and consequently produces a slight lowering of temperature from 65·3° to 61·2°. At I (61·2°), this binodal surface touches another binodal surface

at a second critical point; the two critical points then disappear and with lowering of temperature two binodal curves are obtained for any one temperature which have their end points not on the same base of the triangle but on S—W and P—W. The appearance of the second binodal area is due to the fact that the metastable binodal surface cuts the saturation surface of salicylic acid and has thus a stable portion. G → H and J → H give the com-

Fig. 5.

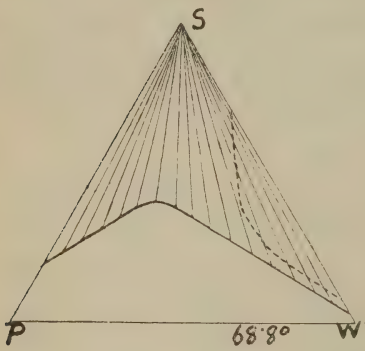
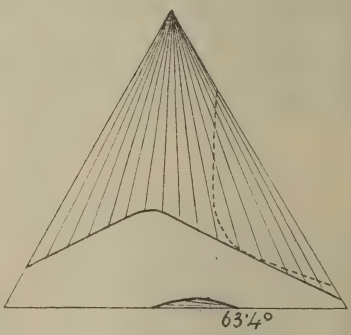


Fig. 6.



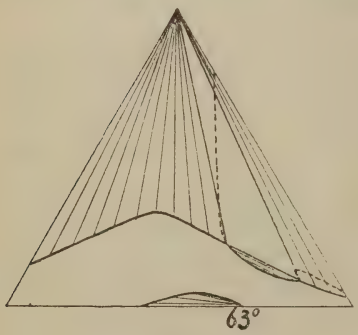


Fig. 7.

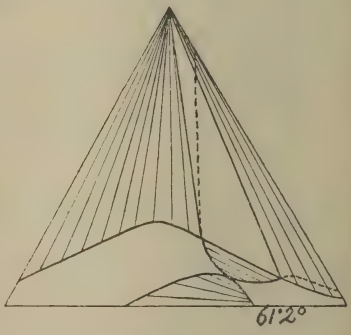


Fig. 8.

position and temperature of the univariant points where solid salicylic acid is in equilibrium with two liquid layers; again we have a curve showing the transition of the melting point under the liquid, but in this case the solid phase which melts is the third component. At H, the metastable binodal surface touches the saturation surface of salicylic acid internally at a critical point.

The Isotherms.—Certain representative isotherms have been chosen and require little elaboration. The diagrams are to some extent schematic, for it has been necessary to enlarge the con-

ditions in the water corner in order to render them visible; they represent accurately the nature of the phase changes which occur.

It will be seen that the solubility of salicylic acid is much greater in the mixed solvents than in either alone: at 68·8° the solubility of the acid in water is 1·3 g. per 100 g. of solution, in phenol 15·4 g., and at the maximum on the ternary solubility curve, 30·1 g. Below 40·8° solid phenol makes its appearance (see Fig. 11); and below 38·2° (Fig. 12) we have a three-phase area where S and P

Fig. 9.

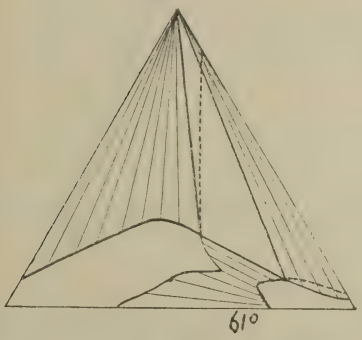
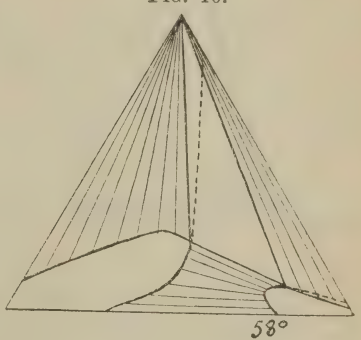


Fig. 10.



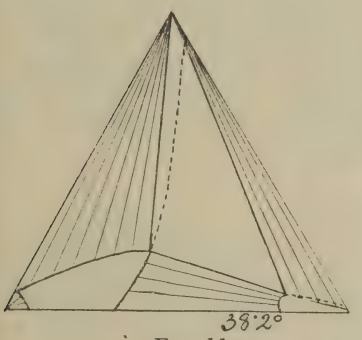


Fig. 11.

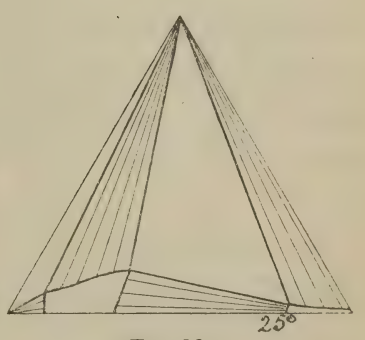


Fig. 12.

are in equilibrium with solution. From 1·7° to — 0·6° P can be in equilibrium with two liquid layers; between these two temperatures at, say, 1·0°, there are three three-phase areas (Fig. 13), the area of two coexistent liquid phases being very small. Below — 0·6° no two liquid layers are observed (Fig. 14) and finally below — 1·3° the system "dries up."

The binodal curve is a distribution curve and the distribution ratio has been determined at 25°. It has been possible to trace only one case where phenol and water have been used as the two immiscible liquids: in this case potassium iodide was found to have

more or less the same molecular weight in both solvents (Riesenfeld, *Z. physikal. Chem.*, 1902, **41**, 347). Table VIII shows that, after correction for the ionisation of the acid in the water layer (a very small effect, since $K = 0{\cdot}001$), the ratio C_w/C_p approaches constancy as the concentration of acid increases.

FIG. 13.

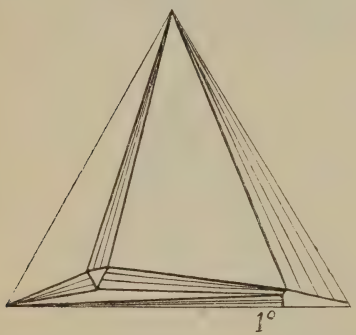
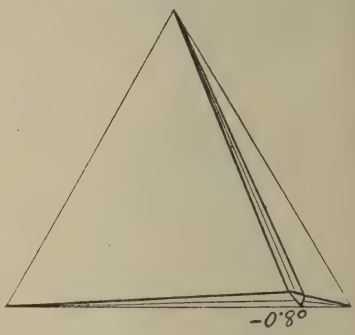


FIG. 14.



Numerical Results.

In the following tables a selection of the more important data for some of the isotherms examined has been made; metastable results throughout are enclosed in square brackets. In order not to complicate the isotherms unduly and to help in the comparison of the temperatures of critical opalescence and solution, the results obtained by the synthetic method are recorded separately. The values given throughout are in weights %.

TABLE V.

The Binodal Curves as obtained by the Synthetic Method.

Under each mixture is given : first, the percentage of phenol in the original mixture, then the percentage additions of salicylic acid, and in the last two rows, the critical solution temperature (C. S. T.) and the temperature of the beginning of critical opalescence (C. Op.).

Mixture B : 9·2% phenol.

% S.	0·0	[5·8	6·8	7·7	11·7	35·4	45·5	58·5	65·4]
C. S. T.°	32·9	58·0	61·0	63·0	68·8	79·0	79·0	68·8	58·0
C. Op.°	32·9	58·0	61·0	63·0	69·5	83·5	79·5	68·8	58·0

Mixture C : 14·6% phenol.

% S.	0·0	3·5	5·9	[6·5	7·2	9·0	15·8	53·4	61·3]
C. S. T.°	56·6	58·0	61·0	61·0	61·0	63·0	68·8	68·8	58·0
C. Op.°	56·8	59·0	62·0	62·5	63·0	65·0	71·0	69·0	58·0

Mixture K : 17·0% phenol.

% S.	0·0	6·5	8·8	[21·5	49·5	57·0	58·0]
C. S. T.°	59·7	61·0	63·0	68·8	68·0	63·0	58·0
C. Op.°	60·0	64·0	65·0	73·0	69·0	63·0	58·0

TABLE V (*continued*).

Mixture D : 20·6% phenol.

% S.	0·0	5·2	5·6	10·8	[28·0	45·3	53·3	54·7]
C. S. T.°	62·0	61·0	61·0	63·0	68·8	68·8	63·0	58·0
C. Op.°	63·2	63·5	64·0	68·0	72·0	68·8	63·0	58·0

Mixture E : 25·0% phenol.

% S.	0·0	1·3	12·6	[45·6	49·3]
C. S. T.°	63·4	63·0	63·0	63·0	58·0
C. Op°.	65·8	65·0	71·5	63·0	58·0

Mixture F : 29·9% phenol.

% S.	0·0	2·2	8·3	11·2	21·0	[39·2	42·4]
C. S. T.°	64·6	63·0	61·0	61·0	63·5	61·0	58·0
C. Op.°	67·6	66·0	69·0	70·0	73·0	61·0	58·0

Mixture G : 34·9% phenol.

% S.	0·0	2·3	8·1	16·0	[22·5	32·6]
C. S. T.°	65·3	63·0	61·0	61·0	61·0	58·0
C. Op.°	67·3	68·0	64·5	62·0	61·0	58·0

Mixture H : 41·7% phenol.

% S.	0·0	2·3	4·8	13·3
C. S. T.°	65·0	63·0	61·0	58·0
C. Op.°	68·3	66·0	64·0	58·0

Mixture I : 50·8% phenol.

% S.	0·0	1·6	4·1
C. S. T.°	62·2	61·0	58·0
C. Op.°	64·4	63·0	59·0

TABLE VI.

Temp. 25·0°.

No.	Phases present.	d_{35}^{25}.	Solution. P.	Solution. W.	Solution. S.	Moist solid residue. P.	Moist solid residue. W.	Moist solid residue. S.
1	S + soln.	1·0008	—	99·78	0·22	—	—	—
2	,,	1·0032	2·42	97·30	0·28	1·3	18·1	80·6
3	,,	1·0057	5·05	94·55	0·40	2·0	21·1	76·9
4	S + L_1 + L_2	1·0080	7·51	91·96	0·53	—	—	—
		1·0640	59·07	32·16	8·77			
5	S + soln.	1·0700	62·66	28·38	8·96	15·9	2·5	76·9
6	,,	1·0761	83·00	10·68	6·32	12·4	7·2	85·1
7	P + S + soln.	1·0785	90·74	4·66	4·60	—	—	—
8	P + soln.	1·0793	93·10	4·41	2·49	—	—	—
9	,,	1·0803	95·70	4·30	—	—	—	—
10	L_1 + L_2	1·0470	70·19	29·81	—	—	—	—
		1·0070	8·43	91·57				
11	,,	1·0500	69·28	30·21	0·51	—	—	—
		1·0072	8·35	91·61	0·04			
12	,,	1·0529	67·41	30·78	1·81	—	—	—
		1·0074	8·23	91·64	0·13			
13	,,	1·0544	65·79	31·09	3·12	—	—	—
		1·0075	8·14	91·65	0·21			
14	,,	1·0610	60·80	31·64	7·56	—	—	—
		1·0078	7·66	91·88	0·46			

Table VII.

Temp. 30·0°.

No.	Phases present.	Solution. P.	W.	S.	Moist solid residue. P.	W.	S.
1	S + soln.	—	99·7	0·26	—	—	—
2	,,	2·6	97·0	0·40	1·4	18·2	80·4
3	,,	7·5	91·9	0·60	—	—	—
4	$L_1 + L_2 + S$	56·6	33·6	9·8	—	—	—
		8·0	91·4	0·64			
5	S + soln.	71·6	18·4	9·8	4·3	1·3	94·4
6	,,	84·9	8·0	7·1	—	—	—
7	,,	88·5	5·6	5·9	25·7	1·6	72·7
8	P + S + soln.	92·5	2·9	4·7	—	—	—
9	P + soln.	94·5	2·9	4·7	—	—	—
10	,,	97·2	2·8	—	—	—	—
11	$L_1 + L_2$	69·3	30·7		—	—	—
		9·1	90·9	—			

Temp. 44·0°.

1	S + soln.	—	99·5	0·46	—	—	—
2	,,	7·8	91·3	1·2	2·8	17·3	79·9
3	$L_1 + L_2 + S$	47·8	38·5	13·6	—	—	—
		8·9	89·7	1·4			
4	S + soln.	49·6	36·0	14·4	25·5	19·9	54·6
5	,,	56·8	27·8	15·4	12·0	6·0	82·0
6	,,	61·9	22·8	15·3	2·2	2·4	95·4
7	,,	70·9	14·8	14·3	27·0	4·3	68·7
8	,,	87·8	4·0	8·2	43·6	2·2	54·2
9	,,	82·8	7·1	10·1	48·6	4·3	47·1
10	,,	92·5	—	7·5	—	—	—
11	$L_1 + L_2$	63·8	35·5	0·72	—	—	—
		10·1	89·8	0·09			
12	,,	59·0	36·7	4·3	—	—	—
		10·4	89·2	0·44			
13	,,	52·6	38·2	9·2	—	—	—
		9·7	89·3	1·0			
14	,,	50·3	38·4	11·3	—	—	—
		9·6	89·2	1·2			
15	,,	64·2	35·8		—	—	—
		10·2	89·8	—			

Temp. 58·0°.

1	S + soln.	—	99·2	0·80	—	—	—
2	,,	7·7	89·9	2·3	1·9	31·6	66·5
3	$L_1 + L_2 + S$	33·2	49·4	17·4	—	—	—
		12·7	83·9	4·3			
4	S + soln.	48·0	29·1	22·9	—	—	—
5	,,	55·6	22·0	22·4	21·1	7·5	71·4
6	,,	73·2	10·0	16·8	—	—	—
7	,,	89·0	—	11·0	—	—	—
8	$L_1 + L_2$	44·2	49·0	6·8	—	—	—
		14·5	83·1	2·4			
9	$L_1 + L_2$	15·3	84·7	—	—	—	—
		55·6	44·4	—			
10	$L_1 + L_2$	[—	96·0	4·0]	—	—	—
		[—	29·4	70·6]			

TABLE VII (*continued*).

Temp. 61·0°.

1	$L_1 + L_2 + S$	28·1	51·9	20·0
		13·5	80·9	5·6
2	$L_1 + L_2$	15·9	77·5	6·6
		28·3	59·7	12·0
3	,,	19·3	74·7	6·0
		23·0	68·5	8·5
4	,,	19·3	75·7	5·0
		29·0	63·0	8·0
5	,,	18·9	81·1	—
		52·8	47·2	—
6	,,	[—	95·4	4·6]
		[—	32·8	67·2]

No solid residues were determined for this and higher temperatures.

Temp. 63·0°.

No.	Phases present.	Solution. P.	W.	S.
1	S + soln.	—	99·0	1·0
2	,,	11·5	83·3	5·2
3	,,	14·2	78·2	7·6
4	$S + L_3 + L_4$	25·2	60·0	15·8
		14·5	77·9	8·5
5	S + soln.	34·2	45·2	20·6
6	,,	87·0	—	13·0
7	Crit. pt. ($L_1 + L_2$)	31·8	65·3	2·9
8	$L_1 + L_2$	43·0	55·1	1·9
		20·5	78·7	0·8
9	,,	23·0	77·0	—
		49·3	50·7	—
10	Crit. pt. ($L_3 + L_4$)	18·0	72·0	10·0
11	$L_3 + L_4$	16·0	75·0	9·0
		22·3	65·2	12·5
12	,,	[—	95·4	4·6]
		[—	31·4	68·6]

Temp. 68·8°.

No.	Phases present.	Solution. P.	W.	S.
1	S + soln.	—	98·7	1·3
2	,,	9·6	84·4	6·0
3	,,	19·9	63·1	17·0
4	,,	38·0	34·4	27·6
5	,,	45·9	24·0	30·1
6	,,	60·0	15·0	25·0
7	,,	84·6	—	15·4

TABLE VIII.

The Distribution of Salicylic Acid between Phenol and Water at 25·0°.

(*The numbers refer to the corresponding points in Table VI.*)

C_w (after correction for ionisation) and C_p, the concentrations in the respective solvents, are given in grams per litre.

No.	C_w.	C_p.	C_w/C_p.	No.	C_w.	C_p.	C_w/C_p.
11	0·38	5·36	0·0709	14	4·57	77·72	0·0570
12	1·27	19·07	0·0668	4	5·28	93·34	0·0565
13	2·07	32·93	0·0629				

My acknowledgments are due to Professor F. G. Donnan, F.R.S., for his kindly help and guidance; and to the Research Fund Committee of the Chemical Society for a grant which has covered the cost of materials used.

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UNIVERSITY COLLEGE, LONDON. [*Received, May 27th*, 1925.]

CCLXIII.—*Carboxycamphoranilic Acids.*

By Mahan Singh and Ram Singh.

Tingle and his co-workers (*Amer. Chem. J.*, 1907, **37**, 596; **38**, 642; 1908, **39**, 1892), as a result of their researches on the intramolecular rearrangement of phthalamic acids, conclude that the change of these acids into phthalimides

$$C_6H_4<\begin{matrix}CO\cdot NH\cdot C_6H_4R\\CO_2H\end{matrix} \rightarrow C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot C_6H_4R+H_2O$$

is dependent on the following factors : (1) the nature of the group R, the stability of the acid increasing as R becomes more negative (stability : $CO_2H > NO_2 > OH >$ halogens); (2) the nature of the amine, the amine being more active, the more strongly positive it is; (3) the temperature; (4) the presence of a solvent such as ethyl alcohol.

The reactions of camphoric anhydride with *o*-, *m*-, and *p*-aminobenzoic acids have now been investigated. They proceed thus :

$$C_8H_{14}<\begin{matrix}CO\\CO\end{matrix}>O+H_2N\cdot C_6H_4\cdot CO_2H = C_8H_{14}<\begin{matrix}CO\cdot NH\cdot C_6H_4\cdot CO_2H.\\CO_2H\end{matrix}$$

The carboxycamphoranilic acids produced are very stable and have not been converted into camphorimides at various temperatures, in various solvents, or by treatment with mild dehydrating agents such as fused sodium acetate and anhydrous sodium sulphate. Hence it appears that if the imide is formed at all, it is so unstable that it is immediately hydrolysed. This may be due to the extreme negativity of the carboxyl group.

The condensation product consists of only one acid in each case; whether it is the α- or the β-camphoranilic acid (compare Singh and Biswas, J., 1924, **125**, 1895) has not been determined.

With regard to the optical rotations of the three carboxycamphoranilic acids, (1) the *o*-carboxy-compound gives negative values; (2) a regularity can be observed between the molecular rotation and the position of the carboxyl group. In all solvents, the order is $p > m > o$; (3) for a given acid in different solvents, the rotatory power diminishes in the order : methyl alcohol, ethyl alcohol, acetone, methyl ethyl ketone. The dielectric constants of these solvents are 35·4, 20·8, 21·5, and 17·8, respectively. The rotatory power, therefore, is lowest in the solvent which has the lowest dielectric constant.

Experimental.

Condensation of Camphoric Anhydride with Aminobenzoic Acids. General Method.—Camphoric anhydride and the aminobenzoic acid (equal mols.) are heated together with fused sodium acetate. The product is dissolved in 80% alcohol (alcohol in the case of the

m-carboxy-compound) and precipitated by the addition of water and scratching, being decolorised by charcoal and by repetition of the process if necessary.

2′-*Carboxycamphoranilic acid*, $CO_2H{\cdot}C_8H_{14}{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H$ (temperature of condensation, 125—130°; time, 3 hours. The yield is seriously affected by variation in temperature, being almost nil above 160°) separates in crystals containing $3H_2O$. It melts at 75—80°, then shrinks, solidifies, and finally melts at 199—200°. It is soluble in ethyl alcohol, methyl alcohol, or acetone, and sparingly soluble in benzene or chloroform (Found : C, 55·0; H, 7·1; N, 3·65; equiv., by titration with NaOH, 187·5. Found, in material heated at 75—80° for 1 hour : C, 64·4; H, 6·8. $C_{17}H_{21}O_5N,3H_2O$ requires C, 54·7; H, 7·2; N, 3·75%; equiv., dibasic, 186·5. $C_{17}H_{21}O_5N$ requires C, 63·95; H, 6·6%).

3′-*Carboxycamphoranilic acid* (temperature of condensation, 160°; time, 3 hours; yield nearly quantitative) is a white, amorphous powder, m. p. 249°, which is soluble in ethyl alcohol, methyl alcohol, or acetone, but insoluble in benzene, chloroform, or ether (Found : C, 63·7; H, 6·9; N, 4·5; equiv., 161. $C_{17}H_{21}O_5N$ requires C, 63·95; H, 6·6; N, 4·4%; equiv., 159·5).

4′-*Carboxycamphoranilic acid* (temperature of condensation, 140—145°; time, 4 hours; yield 95%) separates as a white, amorphous mass which melts at 149—150°, shrinks, re-solidifies, and finally melts at 212°. It is slightly soluble in water, readily soluble in ethyl alcohol, methyl alcohol, or acetone, but only very sparingly so in benzene, ether, or chloroform (Found : C, 60·05; H, 7·4; N, 4·2; equiv., 169·5. Found, in material heated for 1 hour at 135—145° : equiv., 160. $C_{17}H_{21}O_5N,H_2O$ requires C, 60·5; H, 6·8; N, 4·15%; equiv. 168·5. $C_{17}H_{21}O_5N$ requires equiv., 159·5).

Molecular Rotations of the Carboxycamphoranilic Acids.

Solvent.	Conc. g./25 c.c.	Temp.	α_D.	$[\alpha]_D$.	$[M]_D$.
	2′-Carboxycamphoranilic acid, $C_{17}H_{21}O_5N,3H_2O$.				
MeOH	0·0798	18°	−1·00°	−157°	−584°
EtOH	0·0974	17	−1·20	−154	−574
Me_2CO	0·1624	17	−1·92	−148	−551
MeEtCO	0·1294	17	−1·08	−104·5	−390
	3′-Carboxycamphoranilic acid, $C_{17}H_{21}O_5N$.				
MeOH	0·1309	19	+1·53	+146	+466
EtOH	0·0962	17	1·04	135	431
Me_2CO	0·1084	17	1·12	129	412
MeEtCO	0·0714	17	0·56	98	313
	4′-Carboxycamphoranilic acid, $C_{17}H_{21}O_5N,H_2O$.				
MeOH	0·0744	19	+1·52	+255	+860
EtOH	0·1155	17	1·98	214	722
Me_2CO	0·1046	17	1·76	210	709
MeEtCO	0·0820	17	1·08	165	555

The readings were taken in a 2-dcm. tube within 30 minutes of making up the solution. There was no mutarotation.

The authors desire to thank Dr. H. B. Dunnicliff for guidance and practical help during this investigation.

GOVERNMENT COLLEGE,
LAHORE, INDIA. [*Received, April 15th*, 1925.]

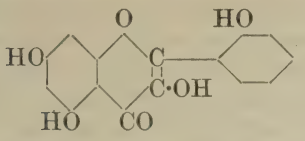
CCLXIV.—*A Synthesis of Datiscetin.*

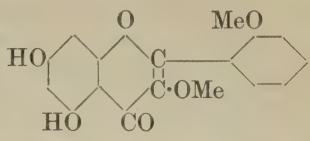
By JAN KALFF and ROBERT ROBINSON.

DATISCIN was isolated by Braconnot in 1816 (*Ann. Chim. Phys.*, **3**, 277) from the leaves of the Bastard Hemp, *Datisca cannabina*, but his largely correct description was ignored and datiscin regarded as identical with inulin until the accurate work of Stenhouse (*Ann. Ch. Pharm.*, 1855, **98**, 166; *Chem. Gaz.*, 1856, No. 318) re-established the individuality of the compound, which he isolated from the roots of the plant. Stenhouse showed that on hydrolysis with acids datiscin yields glucose and datiscetin, $C_{30}H_{10}O_{12}$ (C = 6; O = 8), which by fusion with potassium hydroxide gives salicylic acid or by boiling with dilute nitric acid is changed into nitrosalicylic acid. Roots of *Datisca* from Kew Gardens were examined by Schunck and Marchlewski (*Annalen*, 1893, **277**, 266), who concluded that datiscin is a rhamnoside. The datiscetin isolated in the course of that work had m. p. 237° and differed in some of its properties from the datiscetin of Stenhouse. Fortunately, a small specimen of the material has been preserved in the Schunck Collection housed in the Chemistry Department of this University, and we are of the opinion that it consists essentially of datiscetin mixed with galangin (see p. 1972). It seems possible that the datiscin from the Kew roots was a mixture of galangin rhamnoside and datiscetin glucoside.

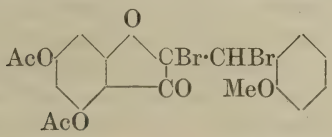
Korczyński and Marchlewski (*Bull. Acad. Sci. Cracovie*, 1906, A, 95; 1907, A, 124) again isolated datiscin, from *Datisca* roots from the Punjab, and showed that it gives glucose on hydrolysis. Moreover, after removal of a methoxyl-containing substance, datiscetin, $C_{15}H_{10}O_6$, m. p. 268—269°, was obtained and characterised and this was clearly the true datiscetin of Stenhouse. From the reactions of datiscetin and the fact that it yields phloroglucinol as well as salicylic acid on fusion with potassium hydroxide, Leškiewicz and Marchlewski (*ibid.*, 1914, A, 218; *Ber.*, 1914, **47**, 1599) drew the conclusion that the substance is 3 : 5 : 7 : 2′-tetrahydroxyflavone (I). The 3 : 5 : 7-trimethyl ether of this flavonol

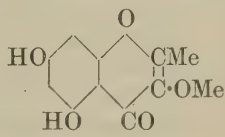
has been synthesised by Bargellini and Peratoner (*Gazzetta*, 1919, **49**, ii, 64), who employed the methods of von Kostanecki, but the derivative has not yet been related to natural datiscetin.

(I.) 

 (II.)

The synthesis now described is an application of the method of Allan and Robinson (J., 1924, **125**, 2192) already used by the present authors (this vol., p. 181) for the syntheses of galangin monomethyl ether and myricetin. ω-Methoxyphloracetophenone (Slater and Stephen, J., 1920, **117**, 316) reacts at 180° with *o*-methoxybenzoic anhydride and sodium *o*-methoxybenzoate to give a product which yields *datiscetin* 3 : 2′-*dimethyl ether* (II) on hydrolysis. On demethylation with hydriodic acid, datiscetin (I) was obtained and we are greatly indebted to Professor Marchlewski for specimens of natural datiscetin and some of its derivatives which have enabled us to make the necessary direct comparisons.

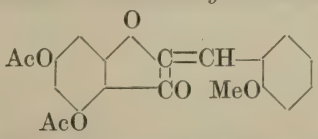
(III.) 

 (IV.)

In some earlier experiments an attempt was made to apply the von Auwers flavonol synthesis (compare *Ber.*, 1915, **48**, 85) to the case of datiscetin. The *compound* III was obtained without difficulty, but no trace of a flavonol could be isolated from the products of its decomposition with alkaline solutions. An attempt was also made to synthesise datiscetin 3-monomethyl ether and accordingly ω-methoxyphloracetophenone was brought into reaction with *o*-acetoxybenzoic anhydride and sodium *o*-acetoxybenzoate. Curiously enough, the acetoxy-groups alone function and we found that the product was 3-*methoxy*-5 : 7-*dihydroxy*-2-*methylchromone* (IV).

Experimental

2-o-*Methoxybenzylidene*-4 : 6-*diacetoxycoumaranone*,



—A satisfactory yield of the methyl ether was obtained by treating salicylaldehyde with methyl sulphate (5 mols.) and aqueous sodium

hydroxide at about 40°. A mixture of *o*-methoxybenzaldehyde (4·1 g.), 4 : 6-dihydroxycoumaranone (5 g.) (Sonn, *Ber.*, 1917, **50**, 1265), and acetic anhydride (90 c.c.) was boiled for 2¼ hours. The product was added to hot water (500 c.c.) and on stirring the oil solidified. The substance crystallised from acetic acid in yellow prisms, m. p. 174° (yield 55%) (Found : C, 65·3; H, 4·5. $C_{20}H_{16}O_7$ requires C, 65·2; H, 4·4%). This substance is insoluble in dilute aqueous sodium hydroxide and gives no coloration with alcoholic ferric chloride. It is sparingly soluble in alcohol or benzene and readily soluble in chloroform. The *dibromide* (formula III) was obtained by the addition with cooling and stirring of bromine (2·4 g.) in chloroform (15 c.c.) to a solution of the methoxybenzylidenediacetoxycoumaranone (5·5 g.) in chloroform (25 c.c.). Evolution of hydrogen bromide did not occur and, after 45 minutes, the substance was precipitated by light petroleum (80 c.c.) and rapidly crystallised from much hot alcohol, separating in small, colourless prisms, m. p. 163° (decomp.) (Found : Br, 31·2, 31·1. $C_{20}H_{16}O_7Br_2$ requires Br, 30·3%). As frequently observed in similar cases, some nuclear bromination has clearly occurred.*

3 : 2′-*Dimethoxy*-5 : 7-*dihydroxyflavone* (II).—*o*-Methoxybenzoic acid of satisfactory purity being somewhat difficult to obtain, an aqueous alkaline solution of salicylic acid was shaken with methyl sulphate (2—3 mols.), the acids isolated, the mixture esterified, and washed with aqueous sodium hydroxide to remove ethyl salicylate. The neutral ester was then hydrolysed.

Comparison of the different processes available for the preparation of *o*-methoxybenzoic anhydride (Rule and Paterson, J., 1924, **125**, 2161) showed that the following is the most convenient (compare D.R.-P. 201325). A 20% solution of carbonyl chloride (1 mol.) in benzene was gradually added with careful cooling to one of the acid (2 mols.) and pyridine (1 mol.) in the same solvent. After 2 hours, the mixture was treated with crushed ice and very dilute sulphuric acid, when the precipitate dissolved. The benzene solution was then further agitated with ice and dilute aqueous sodium carbonate for ½ hour, dried, and the solvent removed by distillation in a vacuum. The residue solidified and was sufficiently pure for most purposes (yield 85%). The product obtained by heating a mixture of ω-methoxyphloracetophenone (5 g.), sodium *o*-methoxybenzoate (7·5 g.), and *o*-methoxybenzoic anhydride (19 g.)

* On prolonged contact with dry methyl alcohol the colourless dibromide changed to yellow prisms which fall to a yellow powder, m. p. 192–193°, at 50–60° [Found: OMe, 7·3. $C_{19}H_{12}O_6Br(OMe)$ requires OMe, 6·95%]. It appears, therefore, that the elements of hydrogen bromide are eliminated and that this process is not accompanied by the introduction of further methoxyl groups.

for 3 hours at 180° was hydrolysed with potassium hydroxide (8·5 g.) in aqueous or alcoholic solution. The phenol, precipitated as a viscous, brown mass by saturating the diluted solution with carbon dioxide, was again treated with aqueous potassium hydroxide on the steam-bath and after isolation as before could be crystallised from aqueous acetic acid (yield 6 g. or 75%). This product was acetylated by treatment with boiling acetic anhydride in presence of sodium acetate. The *diacetyl* derivative crystallised from methyl alcohol in colourless, flat, pointed needles, m. p. 141·5—142·5° (corr.) (Found : C, 63·1; H, 4·5. $C_{21}H_{18}O_8$ requires C, 63·3; H, 4·5%) and was hydrolysed by gently heating with aqueous potassium hydroxide. The datiscetin dimethyl ether, obtained by saturation of the solution with carbon dioxide, crystallised from alcohol in almost colourless, glistening needles, m. p. 218—219° (corr.) [Found : MeO by micro-Zeisel, 19·7. $C_{15}H_8O_4(OMe)_2$ requires MeO, 19·7%]. The yellow solution in sulphuric acid gradually acquires a weak green fluorescence and a yellow solution results when a few drops of a mineral acid are added to a suspension of the dimethyldatiscetin in acetic acid. An alcoholic solution gives a blackish-green coloration with ferric chloride. Mordant dyeing properties were not observed.

Datiscetin (I).—A mixture of 5 : 7-diacetoxy-3 : 2′-dimethoxyflavone (1 g.) and hydriodic acid (15 c.c.; *d* 1·7) was boiled for 30 minutes, and the hot solution filtered (Jena sintered glass) and allowed to cool. The dark yellow crystals of the hydriodide were collected, decomposed by very dilute sulphurous acid, and crystallised from alcohol. The m. p. was at first 260°, but by continued recrystallisation a product, m. p. 276° (corr.), was ultimately obtained in long, pale yellow needles. The specimen of natural datiscetin which was available had m. p. 270·5—271·5° (corr.) and an intimate mixture of the two specimens melted at 273—274° (corr.). The reactions and dyeing properties of the two products were identical. The tetra-acetyl derivative, prepared in the usual manner, crystallised from alcohol in large, colourless, glistening prisms, m. p. 141° (corr.) (Found : C, 60·8; H, 4·0. Calc. for $C_{23}H_{18}O_{10}$, C, 60·8; H, 4·0%). Korczyński and Marchlewski (*loc. cit.*) give 138° (uncorr.) as the m. p. of datiscetin tetra-acetate. The synthetical specimen was also benzoylated by following the method of Korczyński and Marchlewski (*loc. cit.*); the product crystallised from 90% acetic acid in star-shaped aggregates of small needles, m. p. 191—192° (corr.), and at the same temperature when mixed with a specimen prepared from natural datiscetin.

3 : 7 : 2′-*Trimethoxy*-5-*hydroxyflavone*.—Datiscetin dimethyl ether (1 mol.) was methylated by means of methyl iodide (4 mols.) and

potassium hydroxide (4 mols.) in boiling methyl-alcoholic solution for 12 hours. The product crystallised from methyl alcohol in long, colourless needles, m. p. 111—112·5° [Found : MeO, 28·1. $C_{15}H_7O_3(OMe)_3$ requires MeO, 28·3%]. This substance is sparingly soluble in cold methyl alcohol and gives a dull brownish-green coloration with ferric chloride. It is insoluble in cold aqueous sodium hydroxide and on boiling the material becomes yellow but does not dissolve.

3-*Methoxy*-5 : 7-*dihydroxy*-2-*methylchromone* (IV).—A mixture of ω-methoxyphloracetophenone (5 g.), *o*-acetoxybenzoic anhydride (D.R.-P. 201325) (23 g.) and sodium *o*-acetoxybenzoate (9 g.) was heated at 160° for 4·5 hours and then worked up as described in the case of datiscetin dimethyl ether. The phenolic product crystallised from aqueous alcohol in long, pale yellow, glistening needles, m. p. 223—224° (corr.) [Found : MeO, 12·8; loss at 90°, 7·3; in material dried at 90°; MeO, 13·8; *M* by micro-Rast, 208, 228. $C_{10}H_7O_4(OMe),H_2O$ requires MeO, 12·9; H_2O, 7·3%. $C_{10}H_7O_4(OMe)$ requires MeO, 14·0%; *M*, 222]. The substance exhibited the properties of a hydroxylated chromone and we confirmed our view of its nature by the following more rational synthesis. A mixture of ω-methoxyphloracetophenone (3 g.), fused sodium acetate (6 g.), and acetic anhydride (12 c.c.) was heated (oil-bath at 170°) for 4·5 hours, and the chromone isolated in good yield in the usual manner. After crystallisation from alcohol, the substance had m. p. 223—224° (corr.), alone or mixed with the specimen obtained from *o*-acetoxybenzoic acid.

The Occurrence of Galangin in the Root of Datisca cannabina.

The specimen labelled *datiscetin* in the Schunck Collection crystallised from aqueous alcohol in pale yellow needles, m. p. 235—240° with softening from 220°. Its behaviour with solvents, alkaline solutions, mineral acids, potassium acetate and ferric chloride in alcoholic solution closely resembled that of datiscetin and the dyeing properties of the two substances were also identical. There was, however, one striking difference in that the yellow solution in sulphuric acid, at first non-fluorescent, quickly acquired a striking violet fluorescence which was different in tone from the bluer fluorescence due to kaempferol and was entirely distinct from that due to datiscetin. The micro-analyses which we carried out led to no definite conclusion except that methoxyl groups are not present. The substance is hydrated and contains relatively less oxygen than datiscetin. It was then shown by qualitative tests that fusion with potassium hydroxide yields phloroglucinol and that picric acid is produced when the substance is boiled with nitric acid. The clue to

the nature of the material was found in the observation that galangin gives a yellow solution in sulphuric acid which soon develops a brilliant violet fluorescence that is but slightly dulled by the addition of a relatively large amount of datiscetin. The appearance of the sulphuric acid solution of a mixture of synthetical galangin and datiscetin was identical with that of the Schunck specimen dissolved in the same solvent. The following observations were then made under similar conditions: Schunck-datiscetin, m. p. 220—240°; mixed with datiscetin, m. p. 225—245°; mixed with more datiscetin, m. p. 250—260°; mixture of galangin and datiscetin, m. p. 240—255°; the last with more galangin, m. p. 223—240°; the last mixed with Schunck-datiscetin, m. p. 220—238°. A mixture of equal parts of galangin and datiscetin was crystallised from aqueous alcohol and prisms and needles were obtained. The solution was then gently heated to dissolve the needles, filtered, and allowed to cool. The apparently homogeneous needles, m. p. about 240° with previous softening, contained both galangin and datiscetin and closely resembled Schunck-datiscetin in appearance and in the fluorescence of a solution in sulphuric acid.

The authors wish to thank the Royal Society for a grant which has defrayed a part of the expense of the investigation and they also express their gratitude to the Ramsay Memorial Fellowship Trust for a Fellowship (Netherlands) which has enabled one of them to take part in the research.

THE UNIVERSITY, MANCHESTER. [*Received, June 18th*, 1925.]

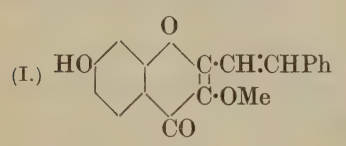
CCLXV.—*The Synthesis of certain 2-Styrylchromonol Derivatives.*

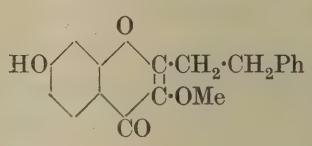
By ROBERT ROBINSON and JUNZO SHINODA.

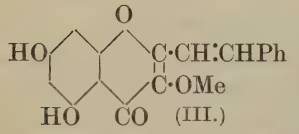
JUST as the difference in composition between successive members of the series of naturally occurring fatty acids is C_2H_4, so it would seem that the increment most common among plant products of the aromatic groups is C_2H_2. Thus benzoic acid and cinnamic acid are associated in many cases and piperic acid represents the next member of the series. Moreover, whilst methyl and propenyl or allylbenzene derivatives are of frequent occurrence, it is less usual to encounter derivatives of ethylbenzene among the constituents of plants.* For this reason we consider it probable that repre-

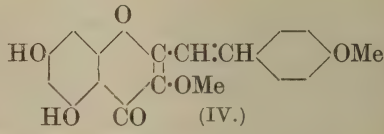
* There are, of course, exceptions to this rule, but many of the natural products with a side-chain comprising two carbon atoms have an obvious relation to more complex substances. Thus hordenine, adrenaline and mezcaline are probably derived by decarboxylation of derivatives of phenylalanine.

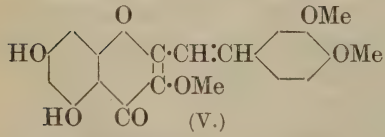
sentatives of the styrylchromones occur in nature and it may be pointed out that fukugetin, $C_{17}H_{12}O_6$ (Perkin and Phipps, J., 1904, **85**, 58), may be a tetrahydroxystyrylchromone related to luteolin, whilst pratensol, $C_{17}H_9O_2(OH)_3$ (Power and Salway, J., 1910, **97**, 231), may be similarly related to apigenin. It is significant that pratensol was found among the constituents of *Trifolium pratense* in company with undoubted flavone derivatives such as quercetin and *iso*rhamnetin, with pratol, probably a hydroxymethoxyflavone, and with a compound, $C_{15}H_7O_3(OH)_3$, isomeric with kaempferol. In the hope of making a contribution to this subject we have synthesised some styrylchromone derivatives which are, however, related to flavonols rather than to flavones. The method adopted was that indicated by Allan and Robinson (J., 1924, **125**, 2192) and utilised by Kalff and Robinson (preceding paper) in the synthesis of methylgalangin, datiscetin, and myricetin. In the simplest example a mixture of ω-methoxyresacetophenone, cinnamic anhydride, and sodium cinnamate is heated at about 180° and after hydrolysis of the product, 7-*hydroxy*-3-*methoxy*-2-*styrylchromone* (I) can be isolated. On reduction with hydrogen in presence of palladium a *dihydro*-derivative (II) is obtained, and the constitution of this substance is confirmed by its synthesis from ω-methoxyresacetophenone, β-phenylpropionic anhydride, and sodium β-phenylpropionate. In a similar manner the compounds III and IV were obtained from ω-methoxyphloracetophenone and the appropriate cinnamic acid derivatives.

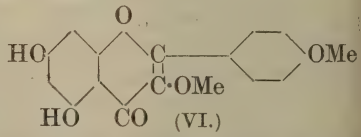












The compounds I, II, and III could be demethylated in the usual way by means of hydriodic acid and we have thus, in the last-mentioned case, obtained the styryl analogue of galangin. Unfortunately no crystalline material could be isolated from the products of demethylation of IV and V, so that we have not been

able to examine the styryl analogues of kaempferol and quercetin. Should these substances be encountered in the examination of material of natural origin, they could be recognised by means of their products of methylation under specified conditions. Both IV and V yield monomethyl ethers when shaken in aqueous alkaline solution with methyl sulphate. There can be little doubt that, as in the case of quercetin, it is the hydroxyl in position 5 which is resistant to the methylating agent. Direct comparison shows that the styryl compounds are more intensely coloured than the corresponding flavones and as mordant dyestuffs they are characterised by much greater tinctorial power. Before we were acquainted with the difficulty of demethylating the compound IV, it seemed desirable to acquire a specimen of kaempferol for purposes of comparison. The simplest plan was to adopt the new method of synthesis, and a kaempferol dimethyl ether (VI) was prepared from ω-methoxyphloracetophenone, anisic anhydride, and sodium anisate. On demethylation, kaempferol, identical with the natural product, was readily obtained. This flavonol has been previously synthesised by von Kostanecki and Tambor (*Ber.*, 1904, **37**, 792) and von Kostanecki, Lampe, and Tambor (*ibid.*, p. 2096).

Experimental.

7-*Hydroxy*-3-*methoxy*-2-*styrylchromone* (I).—A mixture of ω-methoxyresacetophenone (4 g.) (Slater and Stephen, J., 1920, **117**, 313), sodium cinnamate (7·5 g.), and cinnamic anhydride (16 g.) was heated (oil-bath at 180—185°) for 3 hours. The product was hydrolysed by boiling with a mixture of potassium hydroxide (8·5 g.), alcohol (100 c.c.), and a little water for 30 minutes. The alcohol was removed by distillation from the steam-bath and sufficient water added to dissolve the residue, the solution being then saturated with carbon dioxide. The yellow precipitate was crystallised several times from acetic acid and dried (4·5 g.) (Found : C, 73·4; H, 4·9. $C_{18}H_{14}O_4$ requires C, 73·5; H, 4·7%). This compound is sparingly soluble in alcohol and acetic acid and crystallises in long, pale yellow needles, m. p. 250°. It develops no coloration with alcoholic ferric chloride and its bright yellow solution in aqueous sodium hydroxide is not fluorescent. The intense yellow solution in sulphuric acid exhibits a vivid green fluorescence.

3 : 7-*Dihydroxy*-2-*styrylchromone* (corresponding with I).—The methyl ether just described was treated with an excess of boiling hydriodic acid (*d* 1·7) for 30 minutes in a stream of carbon dioxide, the mixture added to dilute sulphurous acid, and the bright yellow substance crystallised from methyl alcohol and acetic acid (Found :

C, 72·8; H, 4·5. $C_{17}H_{12}O_4$ requires C, 72·8; H, 4·2%). The woolly needles separating from methyl alcohol have m. p. 257° and the yellow solutions in aqueous sodium hydroxide and in sulphuric acid exhibit green fluorescence. The coloration with alcoholic ferric chloride is dark brownish-green. On an aluminium mordant * a bright and full lemon-yellow colour was produced, whereas 3 : 7-dihydroxyflavone exhibits very poor affinity and the silk is just coloured a pale yellow. On a chromium mordant the styryl compound gives an intense golden-yellow colour, whilst the related flavonol gives a much paler greenish-yellow. On an iron mordant both substances give a deep cinnamon-brown shade. The differences observed are not merely of intensity but also of tone. In order to obtain 3 : 7-dihydroxyflavone for this comparison we demethylated 7-hydroxy-3-methoxyflavone (Allan and Robinson, *loc. cit.*) in the usual manner by means of hydriodic acid; the product, after crystallisation from methyl alcohol, acetic acid, and finally from ethyl acetate, formed pale yellow, glistening, flat needles, m. p. 258° (Found : C, 66·4; H, 4·7; loss at 100° in a high vacuum, 6·9. $C_{15}H_{10}O_4,H_2O$ requires C, 66·2; H, 4·4; H_2O, 6·6%). von Kostanecki and Stoppani (*Ber.*, 1904, **37**, 1180) have previously obtained this substance from its 7-methyl ether, but they do not state that it crystallises with $1H_2O$.

β-*Phenylpropionic Anhydride.*—We have found the method adopted by Liebermann (*Ber.*, 1883, **21**, 3372) for the preparation of cinnamic anhydride to be expeditious and have employed it in other cases. A solution of β-phenylpropionic acid (15 g.) in acetic anhydride (30 g.) was boiled for 4 hours and then distilled; 10 g. of a viscous liquid, b. p. 216—217°/14 mm., were obtained (Found : C, 76·3; H, 6·7. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%).

7-*Hydroxy*-3-*methoxy*-2-β-*phenylethylchromone* (II).—(A) 7-Hydroxy-3-methoxy-2-styrylchromone (1 g.) dissolved in acetic acid (200 c.c.) was reduced by shaking with hydrogen, aqueous palladous chloride (10 c.c. of 1%) having been added to the mixture. Absorption ceased after about 2 hours. The product crystallised from aqueous acetic acid in colourless prisms, m. p. 186—187° (Found : C, 72·6; H, 5·5. $C_{18}H_{16}O_4$ requires C, 72·9; H, 5·4%). The yellow solution in sulphuric acid exhibits a blue fluorescence.

(B) ω-Methoxyresacetophenone (2 g.), sodium β-phenylpropionate, and β-phenylpropionic anhydride (8 g.) were mixed and heated

* All the dye-trials were made on silk. The aluminium mordant was prepared from alum and sodium carbonate and fixed with sodium silicate and it was found to be essential to exclude even traces of iron. The chromium mordant was prepared from basic chrome alum, fixed with sodium silicate, and the fabric was iron-mordanted by successive treatment with a solution of ferric nitrate and a solution containing soap and sodium carbonate.

at about 180° for 3 hours. The product, isolated as in the case of the styryl analogue, crystallised from aqueous acetic acid in colourless prisms, m. p. 186—187°, which was not depressed by admixture with the specimen prepared by the method (A).

3 : 7-*Dihydroxy*-2-β-*phenylethylchromone*, obtained by demethylation of the 3-methyl ether by means of boiling hydriodic acid, crystallises from aqueous alcohol in almost colourless, prismatic needles, m. p. 169° (Found in material dried at 100° with change of appearance: C, 68·0; H, 5·4. $C_{17}H_{14}O_4$ requires C, 68·0; H, 5·3%). The substance is readily soluble in most organic solvents and its solution in aqueous sodium hydroxide is colourless. It is devoid of any trace of mordant dyeing properties. The yellow solution in sulphuric acid exhibits a blue fluorescence and the ferric chloride coloration in alcoholic solution is dark violet.

3-*Methoxy*-5 : 7-*dihydroxy*-2-*styrylchromone* (III).—A good yield of this compound was obtained by following in every detail the method described for the preparation of 3-methoxy-7-hydroxy-2-styrylchromone. The yellow substance crystallises from acetic acid in microscopic needles, m. p. 241° (Found: C, 69·8; H, 4·6. $C_{18}H_{14}O_5$ requires C, 69·9; H, 4·5%). The orange-yellow alcoholic solution is coloured brown by the addition of a trace of ferric chloride, and the yellow solution in sulphuric acid shows a green fluorescence which becomes more intense on standing.

3 : 5 : 7-*Trihydroxy*-2-*styrylchromone* (corresponding with III).—The product of demethylation of the foregoing ether crystallised from alcohol in stellar clusters of yellow needles, m. p. 249° (Found in material dried at 100° in a high vacuum: C, 68·7; H, 4·1. $C_{17}H_{12}O_5$ requires C, 68·9; H, 4·0%). The golden-yellow solution in aqueous sodium hydroxide does not fluoresce, but the sulphuric acid solution exhibits strong fluorescence. The shades yielded by galangin on mordanted silk are almost identical with those given by 3 : 7-dihydroxyflavone, and the styryl analogue of galangin now described yields, on an aluminium mordant and on an iron mordant, shades similar to those given by 3 : 7-dihydroxy-2-styrylchromone. On a chromium mordant, however, it yields a bright orange dyeing. The *triacetyl* derivative was obtained by the action of boiling acetic anhydride in presence of fused sodium acetate on the trihydroxystyrylchromone. It crystallises from alcohol in nearly colourless, prismatic needles, m. p. 215—216°.

4-*Methoxycinnamic Anhydride*.—4-Methoxycinnamic acid was obtained in almost quantitative yield by acidification of a diluted mixture of anisaldehyde (1 mol.), malonic acid (2·5 mols.), pyridine (3 mols.), and a few drops of piperidine which had been heated on the steam-bath during 1·5 hours and then boiled. The acid crystal-

lised from boiling water in colourless, prismatic needles, m. p. 173° (recorded in the literature, 171°), and was dehydrated by vigorously boiling with three times its weight of acetic anhydride for 15 hours. After the excess of acetic anhydride and the acetic acid formed had been removed by distillation, the cooled residue solidified and could be directly employed in the chromonol synthesis. The substance crystallises from ethyl acetate in large prisms, m. p. 119—120° (Found : C, 71·3; H, 5·5. $C_{20}H_{18}O_5$ requires C, 71·0; H, 5·3%). The substitution of methoxyl for hydrogen in the *p*-position in benzoic and also in cinnamic acid has the effect of making anhydride formation by this method very noticeably more difficult. It is possible that methoxyl in the *m*-position has an influence in the other direction, since it is more easy to dehydrate veratric acid and 3 : 4-dimethoxycinnamic acid than anisic acid and 4-methoxycinnamic acid.

The following method has also been successfully employed for preparing the anhydride (compare Fischer and Freudenberg, *Ber.*, 1913, **46**, 1124). 4-Methoxycinnamic acid (5 g.) was converted into the *chloride* by gentle heating during about 25 minutes with purified thionyl chloride (25 g.) and removal of excess of the reagent by distillation in a vacuum. The crystalline chloride together with 4-methoxycinnamic acid (4 g.) was dissolved in chloroform, and pyridine (9 c.c.) gradually introduced. The anhydride crystallised and could be isolated after 3 hours by the addition of alcohol and washing with very dilute aqueous ammonia. Recrystallised from ethyl acetate, it had m. p. 119—120° (yield 8 g.).

3 : 4′-*Dimethoxy*-5 : 7-*dihydroxy*-2-*styrylchromone* (IV).—An intimate mixture of ω-methoxyphloracetophenone (4·5 g.), 4-methoxycinnamic anhydride (18 g.), and sodium 4-methoxycinnamate (9 g.) was heated at 180° in a vacuum for 3 hours, and the product hydrolysed by treatment with potassium hydroxide (10 g.) and alcohol (100 c.c.) at the boiling point for ½ hour. The yellow precipitate obtained by saturating the diluted mixture with carbon dioxide, after being washed and dried (yield 90%), crystallised from acetic acid in aggregates of intensely yellow needles, m. p. 228° (Found : C, 66·7; H, 4·2. $C_{19}H_{16}O_6$ requires C, 67·0; H, 4·2%). The orange solution in sulphuric acid exhibits greenish-yellow fluorescence and the yellow solution in alcohol develops a brown coloration with ferric chloride.

3 : 7 : 4′-*Trimethoxy*-5-*hydroxy*-2-*styrylchromone*, the methyl ether of the substance described in the last section, was obtained by shaking the red solution of the phenol in aqueous sodium hydroxide with methyl sulphate until the yellow precipitate no longer dissolved on the addition of more sodium hydroxide. The product was

collected, washed with water, and crystallised from aqueous acetic acid, separating in bright yellow prisms, m. p. 156° (Found: C, 67·6; H, 5·0. $C_{20}H_{18}O_6$ requires C, 67·8; H, 5·1%). This substance is quite insoluble in aqueous sodium hydroxide, even when boiled, but the intensification of the colour from yellow to orange in alcoholic solution on the addition of solid potassium hydroxide indicates the weak phenolic function. It is curious that on diluting such an alcoholic solution with water a clear yellow liquid is obtained and the phenol actually separates completely on boiling, leaving a colourless solution. The alcoholic solution gives a yellowish-brown coloration on the addition of ferric chloride.

3 : 4-*Dimethoxycinnamic Anhydride*.—3 : 4-Dimethoxycinnamic acid is obtained in almost quantitative yield from veratraldehyde by condensation with malonic acid in pyridine–piperidine solution at 100° and it may also be conveniently prepared by the methylation of ferulic acid which is effected by shaking an aqueous alkaline solution with methyl sulphate. Ferulic acid was produced in 80% yield when a mixture of vanillin (50 g.), malonic acid (104 g.), pyridine (140 c.c.), and piperidine (4 c.c.) was heated for 1·5 hours on the steam-bath. The acid, crystallised from hot water, had m. p. 171° (recorded in the literature, 168—169°). A mixture of 3 : 4-dimethoxycinnamic acid (5 g.) and acetic anhydride (10 g.) was vigorously boiled for 5 hours and the acetic acid and excess of acetic anhydride removed by distillation in a vacuum. The residue was dissolved in a little hot benzene and, on cooling, the new anhydride separated. It crystallised from ethyl acetate in colourless needles, m. p. 174—175° (Found: C, 66·4; H, 5·8. $C_{22}H_{22}O_7$ requires C, 66·3; H, 5·5%).

3 : 3′ : 4′-*Trimethoxy*-5 : 7-*dihydroxy*-2-*styrylchromone* (V).—The method of preparation of this substance from ω-methoxyphloracetophenone, 3 : 4-dimethoxycinnamic anhydride, and sodium 3 : 4-dimethoxycinnamate followed exactly the lines of the similar cases described above. The bright yellow substance is readily soluble in alcohol and acetic acid, but may be crystallised from methyl alcohol in fine orange needles (Found: C, 61·7; H, 5·2; loss at 100° in a high vacuum, 5·3. $C_{20}H_{18}O_7,H_2O$ requires C, 61·8; H, 5·3; H_2O, 4·9%). The dried material is yellow and has m. p. 233—234°. The orange solution in sulphuric acid exhibits a weak green fluorescence; the ferric chloride reaction in alcoholic solution is brown; and the alkaline solutions are orange-yellow.

3 : 7 : 3′ : 4′-*Tetramethoxy*-5-*hydroxy*-2-*styrylchromone*.—The phenol last described was mixed with a little water and treated alternately with concentrated potassium hydroxide and methyl sulphate until the solution was no longer red when alkaline. The yellow precipitate

crystallised from alcohol and from ethyl acetate in glistening, yellow leaflets, m. p. 203—204° (Found: C, 65·3; H, 5·2. $C_{21}H_{20}O_7$ requires C, 65·6; H, 5·2%). The behaviour of this compound with aqueous and alcoholic solutions of alkali metal hydroxides and with ferric chloride closely resembled that of 3 : 7 : 4′-trimethoxy-5-hydroxy-2-styrylchromone.

3 : 4′-*Dimethoxy*-5 : 7-*dihydroxyflavone* (VI).—Anisic acid is not completely dehydrated by boiling acetic anhydride in 6 hours, but in 20 hours a good yield of the anhydride is obtained and the process is convenient. The substance isolated as in the example previously described, crystallised from ethyl acetate in needles, m. p. 98—99° (compare Pisani, *Annalen*, 1857, **102**, 284). The preparation of a flavonol derivative from ω-methoxyphloracetophenone (2·5 g.), anisic anhydride (10 g.), and sodium anisate (5 g.) was carried out as in previous cases. The crude product crystallised from aqueous acetic acid in pale yellow platelets with rounded corners, m. p. 234°. The substance exhibits a bronze-like appearance (Found: C, 65·1; H, 4·6. $C_{17}H_{14}O_6$ requires C, 65·0; H, 4·4%). This kaempferol dimethyl ether is sparingly soluble in hot methyl alcohol and gives a violet ferric chloride reaction in alcoholic solution. Its yellow solution in concentrated sulphuric acid exhibits a bright bluish-green fluorescence the intensity of which increases on standing. On demethylation with hydriodic acid (*d* 1·7) in the usual manner, kaempferol was readily obtained. The pale yellow needles deposited from alcoholic solution had m. p. 276—277° and this is the m. p. given by A. G. Perkin (J., 1902, **81**, 585), whereas von Kostanecki and Gordin quote the value 271° (*Ber.*, 1901, **34**, 3723) and von Kostanecki, Lampe, and Tambor (*loc. cit.*) give the m. p. 275° for the synthetical material. The strong greenish-blue fluorescence of the yellow solution in sulphuric acid was observed and the dyeing and other properties were those of kaempferol. The *tetra-acetyl* derivative was prepared and after crystallisation from ethyl alcohol had m. p. 181—182°, but, as stated by A. G. Perkin, when crystallised from methyl alcohol the substance sinters at 116—120° without completely melting, then hardens on further heating and melts at 181—182°. These observations render it certain that the synthetical material is identical with the naturally occurring flavonol called kaempferol.

We desire to thank the Royal Society for a grant which has defrayed a part of the cost of this investigation.

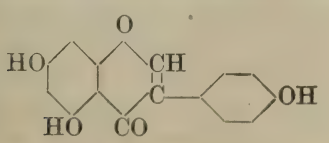
THE UNIVERSITY, MANCHESTER. [*Received, June 23rd*, 1925.]

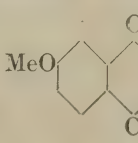
CCLXVI.—*Synthetical Experiments in the* iso*Flavone Group. Part I.*

By Wilson Baker and Robert Robinson.

Whilst derivatives of 2-phenylchromone (flavone) and related substances in various states of oxidation (catechins, cyanomaclurin, butein, hyssopinaglykone, the anthocyanins and anthoxanthins) are found widespread in nature, the occurrence of derivatives of 3-phenylchromone (*iso*flavone) has not yet been definitely proved in any single instance. Nevertheless Finnemore has suggested (*Pharm. J.*, 1910, **31**, 604) that prunetin, $C_{16}H_{12}O_5$, obtained by hydrolysis of the glucoside prunetrin is the methyl ether of a trihydroxy*iso*flavone (I) and the isolation of *p*-hydroxyphenylacetic acid and phloroglucinol from the products of fusion with potassium hydroxide is strong evidence that this view is correct. On demethylation prunetin yields prunetol, $C_{15}H_{10}O_5$, and we are informed by Professor A. G. Perkin that there is a possibility that this substance is identical with genistein, the colouring matter of Dyer's Broom (*Genista tinctoria*) (Perkin and Newbury, J., 1899, **75**, 830; Perkin and Horsfall, J., 1900, **77**, 1310). The following comparison will serve to make clear the basis of this suggestion. Genistein; long, colourless needles from aqueous alcohol, m. p. 291—293°; prunetol, colourless needles from aqueous alcohol, m. p. *ca.* 290° (decomp.): triacetylgenistein, m. p. 197—201°; triacetylprunetol, m. p. 205°: genistein dimethyl ether, colourless leaflets from alcohol, m. p. 137—139°; prunetin monomethyl ether, flat needles, m. p. 145°: acetyl derivative of genistein dimethyl ether, colourless needles, m. p. 202—204°; acetyl derivative of prunetin monomethyl ether, colourless needles, m. p. 202°. In addition it was found that genistein dimethyl ether yields *p*-methoxyphenylacetic acid by hydrolysis with alcoholic potassium hydroxide.

A synthesis of the compound (I) would clearly be of considerable interest and we have decided to attempt it. The present communication is a record of the necessary preliminary investigation of the methods available, and it has been found that though *iso*flavones substituted in position 2 are easy to prepare, the contrary is the case when it is desired to leave this position unsubstituted.

(I.) 

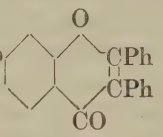


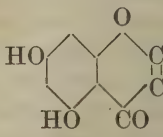
(II.)

The problem is analogous to that presented by the synthesis of

anhydrobrazilic acid, which is also a 3-substituted chromone derivative, but the method which was successful in that case (Perkin and Robinson, J., 1908, **93**, 503) was found to be inapplicable in the present instance. Ultimately 7-methoxy*iso*flavone (II) was synthesised by degradation of its 2-styryl derivative (X) by oxidation with potassium permanganate in pyridine solution and thermal decomposition of the resulting 7-methoxy*iso*flavone-2-carboxylic acid. A synthesis of (I) is thus rendered feasible. 2-Substituted *iso*flavones are quite readily obtained by the interaction of 2 : 4-dihydroxyphenyl benzyl ketone or the corresponding phloroglucinol derivative with a mixture of the anhydrides and sodium salts of carboxylic acids at 170—180° in accordance with a general method. For example, interaction of the former ketone and acetic anhydride and sodium acetate followed by hydrolysis of the product yields 7-*hydroxy*-2-*methyl*iso*flavone* (III), 7-*hydroxy*-3-*phenyl*-*flavone* (IV) is similarly obtained by means of benzoic anhydride and sodium benzoate, whilst 2 : 4 : 6-trihydroxyphenyl benzyl ketone, acetic anhydride, and sodium acetate yield ultimately the iso*flavone* (V).

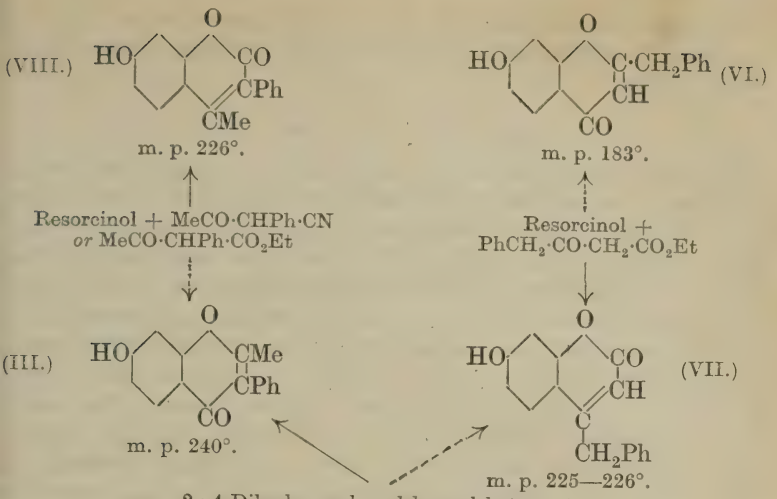
(IV.)





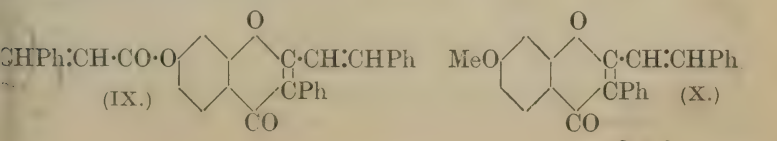
(V.)

A substance which, it was claimed, had the formula (III) has been obtained by Ghosh (J., 1916, **109**, 105) and formulæ (IV) and (V) have been assigned by Jacobson and Ghosh (J., 1915, **107**, 1051) to compounds prepared by them, but the properties of the substances as recorded by these authors do not tally, even approximately, with our observations and there appears to be no possibility that the specimens prepared by the two methods can be identical. Since the synthetical process employed by Ghosh and by Jacobson and Ghosh is essentially that due to von Pechmann and was originally devised for the synthesis of coumarins, it seems possible that all these compounds, including eleven alleged *iso*flavones, are α-pyrones. In regard to the three substances already mentioned, this conclusion is inevitable unless it can be shown that we have taken a wrong view of the course of the reactions described in this communication. No alternative, however, is possible in the case of the compound (IV) and in regard to (III) (with which V is doubtless strictly analogous) the relations included in the annexed scheme demonstrate the correctness of our hypothesis. The dotted arrows show possible courses of the reactions and the full arrows the direction in which they actually proceed :



The condensation of ethyl β-keto-γ-phenylbutyrate and resorcinol yields 7-*hydroxy*-4-*benzylcoumarin* (VII), because the product of the reaction is not identical with the 7-hydroxy-2-benzylchromone (VI) synthesised by Hannach and Kostanecki (*Ber.*, 1902, **35**, 867). The non-identity of (III) and (VII) disposes of the only alternative for (III) and therefore the compound obtained by Ghosh from acetylphenylacetonitrile and resorcinol must have the constitution (VIII). It is possible that the whole of the compounds described by Jacobson and Ghosh and by Ghosh in four papers (*loc. cit.* and J., 1915, **107**, 424, 959) as γ-pyrones are in fact α-pyrones. A further critical examination of this subject is in progress. The question of the mechanism of the chromone synthesis is to some extent answered as the result of the observation that the di-*o*-acetyl derivative of 2 : 4-dihydroxyphenyl benzyl ketone, which is stable to acetic anhydride alone, suffers ring closure under the influence of acetic anhydride and sodium acetate.

The action of cinnamic anhydride and sodium cinnamate (compare the preceding paper) on 2 : 4-dihydroxyphenyl benzyl ketone gave rise to 7-*cinnamoyloxy*-2-*styryl*iso*flavone* (IX), from which (X) and then, as already stated, (II) were derived. The investigation is being extended.



The alkali-metal salts of (IV) exhibit phenomenal colloidal properties, a preliminary account of which is given in the experimental section.

Experimental.

7-*Hydroxy*-2-*methyl*isoflavone (III).—The red solution exhibiting green fluorescence which is obtained after boiling the acetyl derivative (see below) with an excess of dilute aqueous sodium carbonate for 2 hours was acidified and the crystalline precipitate collected (yield—over 90% from 2 : 4-dihydroxyphenyl benzyl ketone). The substance separates from methyl alcohol containing a few drops of water in very pale brownish-yellow needles melting at 240° when rapidly heated (Found : C, 76·3; H, 4·8. $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%). The colourless solutions in aqueous sodium hydroxide and concentrated sulphuric acid exhibit weak blue and bluish-violet fluorescences respectively. The *methyl* ether obtained by interaction with methyl sulphate in aqueous potassium hydroxide solution at about 60° crystallised from aqueous alcohol in nearly colourless needles, m. p. 135·5° (Found : C, 76·7; H, 5·3. $C_{17}H_{14}O_3$ requires C, 76·7; H, 5·3%). The *acetyl* derivative was prepared by heating (oil-bath at 170—180°) a mixture of 2 : 4-dihydroxyphenyl benzyl ketone (10 g.) (Chapman and Stephen, J., 1923, **123**, 404), acetic anhydride (40 c.c.), and anhydrous sodium acetate (10 g.) under reflux for 12 hours. The product was shaken with dilute hydrochloric acid, and the solid crystallised from alcohol in colourless prisms, m. p. 162° (Found : C, 73·6; H, 4·8. $C_{18}H_{14}O_4$ requires C, 73·4; H, 4·8%). The same compound was obtained from 2 : 4-diacetoxyphenyl benzyl ketone (Chapman and Stephen, *loc. cit.*) in a precisely similar manner.

7-*Hydroxy*-4-*benzylcoumarin* (VII).—A solution of resorcinol (2 g.) and ethyl β-keto-γ-phenylbutyrate (2 g.) (Attwood, Stevenson, and Thorpe, J., 1923, **123**, 1762) in concentrated sulphuric acid (10 c.c.) was heated on the steam-bath for 20 minutes. The solid isolated after the addition of water crystallised from alcohol in faintly brown prisms, m. p. 225—226° (Found : C, 76·2; H, 4·9. $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%). The yellow solution in aqueous sodium hydroxide has a blue fluorescence and the colourless solution in sulphuric acid fluoresces bluish-violet.

5 : 7-*Dihydroxy*-2-*methyl*isoflavone (V).—This substance and its derivatives were obtained, in the first place from 2 : 4 : 6-trihydroxyphenyl benzyl ketone (Chapman and Stephen, *loc. cit.*), by methods entirely similar to those used in the case of the resorcinol analogue. The substance crystallises from concentrated alcoholic solution in faintly yellowish-brown prisms, m. p. 228° (Found : C, 71·7;

H, 4·7. $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%). The yellow solution in aqueous alkalis does not exhibit fluorescence.

The *diacetyl* derivative crystallises from alcohol in colourless, silky needles, m. p. 169° (Found: C, 68·0; H, 4·6. $C_{20}H_{16}O_6$ requires C, 68·2; H, 4·6%). The 7-*monomethyl* ether crystallises from methyl alcohol in glistening, colourless needles, m. p. 186—187°, insoluble in aqueous sodium hydroxide but giving a bluish-green coloration with ferric chloride in alcoholic solution. The solutions in concentrated sulphuric acid of this and the two substances last described exhibit weak bluish-green fluorescence.

7-*Hydroxy*-3-*phenylflavone* (7-*Hydroxy*-2-*phenyl*iso*flavone*) (IV).—A mixture of 2 : 4-dihydroxyphenyl benzyl ketone (20 g.), benzoic anhydride (100 g.), and sodium benzoate (10 g.) was heated (oil-bath at 180—190°) for 12 hours, and the product dissolved in alcohol (250 c.c.) and water (50 c.c.) by heating on the steam-bath. A solution of potassium hydroxide (60 g.) in water (100 c.c.) was added, and heating on the steam-bath continued for 15 minutes, after which water (500 c.c.) was added and the phenol precipitated by saturating the solution with carbon dioxide. It is important to follow the above directions in order to ensure the avoidance of the formation of a thick gel through which the gas cannot be passed. The crude product crystallised from ethyl alcohol (800 c.c.) in microscopic needles and on recrystallisation separated in glistening, pale yellow plates, m. p. 270—271° (yield of fully purified material, 20 g.) (Found: C, 80·3; H, 4·6. $C_{21}H_{14}O_3$ requires C, 80·2; H, 4·5%). The pale yellow solution in sulphuric acid exhibits a bluish-green fluorescence. The substance does not appear to dissolve in cold aqueous potassium hydroxide, but this is due to the formation of a gel round each crystal. On heating, a greenish-yellow solution is produced and this sets on cooling to a clear gel. A 1% solution sets to a stiff gel which is with difficulty shaken from a test-tube, whilst even a 0·1% solution gives a weak gel which, with an excess of alkali, will almost permit the inversion of the tube without displacement of the contents. The nature of the gels is very much affected by the concentration of the alkali. The *acetyl* derivative, prepared from the phenol by the action of boiling acetic anhydride for 4 hours, crystallised from acetic acid in pale yellow prisms, m. p. 208—209° (Found: C, 77·4; H, 4·5. $C_{23}H_{16}O_4$ requires C, 77·5; H, 4·5%).

7-*Cinnamoyloxy*-2-*styryl*iso*flavone* (IX).—A mixture of 2 : 4-dihydroxyphenyl benzyl ketone (10 g.), cinnamic anhydride (40 g.), and sodium cinnamate (10 g.) was heated (oil-bath at 170—180°, finally at 215°) for 5 hours. The cooled, ground product was washed with dilute aqueous sodium hydroxide, and the cinnamic anhydride

decomposed by heating on the steam-bath for an hour with alcohol (100 c.c.), water (20 c.c.), and concentrated sulphuric acid (1 c.c.). The solid then obtained on the addition of water was collected, washed with aqueous sodium hydroxide, and crystallised from acetic acid, in which it was sparingly soluble. The pale yellowish-brown prisms, m. p. 213—214°, dissolved in sulphuric acid to an intensely yellow solution exhibiting green fluorescence (Found : C, 81·6; H, 4·8. $C_{32}H_{22}O_4$ requires C, 81·7; H, 4·7%).

7-*Methoxy*-2-*styryl*iso*flavone* (X).—The crude cinnamoyloxy-styryl*iso*flavone from 10 g. of 2 : 4-dihydroxyphenyl benzyl ketone was added to alcohol (100 c.c.) and potassium hydroxide (7·5 g.) dissolved in a little water, and the whole heated for 5 minutes on the steam-bath. Water (100 c.c.) * was added and the phenol contained in the solution was methylated at 60° by the alternate addition of methyl sulphate and concentrated aqueous potassium hydroxide. After the addition of more water the methyl ether was collected (13·9 g.). It crystallised from ethyl alcohol, in which it was sparingly soluble, in pale yellow needles, m. p. 204—205° (Found : C, 81·4; H, 5·0. $C_{24}H_{18}O_3$ requires C, 81·3; H, 5·1%). The deep yellow solution in sulphuric acid has a green fluorescence.

7-*Methoxy*iso*flavone* (II).—7-Methoxy-2-styryl*iso*flavone (2 g.) dissolved in pure pyridine (20 c.c.) was oxidised at 0° in the course of an hour by the slow addition, with stirring and passage of carbon dioxide, of aqueous potassium permanganate (100 c.c. saturated at 15°). The manganese precipitate was brought into solution by sulphur dioxide and after the addition of dilute hydrochloric acid the ether-soluble contents of the liquid were isolated. The crude product was extracted with warm sodium bicarbonate solution, the filtrate acidified, and the organic acids were again collected by ether. The residue mixed with a little copper powder was cautiously heated over a free flame until evolution of carbon dioxide ceased, and the product shaken with aqueous sodium bicarbonate and ether. The neutral oil obtained from the ethereal solution solidified on stirring and the substance crystallised from not too much alcohol in needles, m. p. 155° (Found : C, 75·7; H, 5·1. $C_{16}H_{12}O_3$ requires C, 76·1; H, 4·8%). The colourless solution in sulphuric acid exhibits a blue fluorescence.

The authors desire to thank the Chemical Society for a grant which has defrayed a part of the cost of this investigation.

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* If more water is added, a thick, mucilaginous, colloidal solution results.

CCLXVII.—*Oxidation Products of Oleic Acid. Part II. Degradation of Dihydroxystearic Acid.*

By Arthur Lapworth and Edward Neville Mottram.

Spirondonov (*J. Russ. Chem. Soc.*, 1887, **19**, 646) oxidised dihydroxystearic acid with potassium permanganate, and an examination of the degradation products led to the separation of *n*-octoic, suberic and azelaic acids. Edmed (J., 1898, **73**, 628) carried out further investigations in this direction, but obtained no evidence of the formation of either suberic or *n*-octoic acid. He isolated three main products, namely azelaic, *n*-nonoic and oxalic acids, and assumed that the last-named was produced by the oxidation of the chain of carbon atoms which otherwise would have yielded pelargonic acid. Edmed's conclusion has been generally accepted, but the evidence obtained by the present authors does not support his view. In dilute alkaline solution at the ordinary temperature, *n*-octoic, suberic, and oxalic acids are the main oxidation products in several experiments, and it is necessary to conclude that the oxalic acid is a primary product in the degradation of dihydroxystearic acid and is formed by a splitting between the 8—9 and 10—11 carbon atoms as indicated below.

$$CH_3\cdot[CH_2]_6\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot[CH_2]_6\cdot CO_2H$$

$CH_3\cdot[CH_2]_6\cdot CO_2H$	$CO_2H\cdot CO_2H$	$CO_2H\cdot[CH_2]_6\cdot CO_2H$
n-Octoic acid.	Oxalic acid.	Suberic acid.

In the conditions employed by Edmed, it appears that this mode of oxidation takes place simultaneously with that of the better known type

$$CH_3\cdot[CH_2]_7\cdot CH(OH)\cdot CH(OH)\cdot[CH_2]_7\cdot CO_2H$$

$CH_3\cdot[CH_2]_7\cdot CO_2H$	$CO_2H\cdot[CH_2]_7\cdot CO_2H$
n-Nonoic acid.	Azelaic acid.

Experimental.

1. (a) *Oxidation.* A solution of dihydroxystearic acid (5·0 g.) and caustic soda (10 g.) in water (1000 c.c.) was cooled, ice-cold water (3000 c.c.) added, and the whole well shaken during the addition of 1% aqueous potassium permanganate (2000 c.c.). Oxidation having proceeded at the ordinary temperature for 2½ hours, the solution was decolorised by sulphur dioxide, concentrated hydrochloric acid (100 c.c.) added, and the white, flocculent precipitate of unchanged dihydroxystearic acid filtered off, and washed with water. Traces of liquid fatty acids were removed from the drained

precipitate by washing with a little light petroleum (b. p. 40—60°) and the unchanged dihydroxystearic acid (0·40 g., m. p. 130°) was recovered.

The aqueous filtrate was neutralised with sodium carbonate, concentrated to about 500 c.c., and excess of hydrochloric acid added. The liberated mixed acids, isolated by means of ether,* were distilled with steam to separate the volatile portion; on cooling, the aqueous solution (75 c.c.) in the distillation flask deposited 1·6 g. of crystalline suberic acid, m. p. 137—138°. The mother-liquor on evaporation yielded further small quantities of suberic acid (0·3 g.). The total yield of suberic acid obtained was 1·90 g. (Theory requires 2·47 g.) and the equivalent found was 87·9 ($C_8H_{14}O_4$ requires 87·0), this slightly high value being almost certainly due to traces of octoic acid.

(b) *Examination of dibasic acid for azelaic acid.* The whole of the dibasic acid was warmed with 20—30 c.c. of ether, and the solution allowed to crystallise. The solid which separated (1·5 g.) was removed by filtration, and the mother-liquor evaporated to dryness. This solid was dissolved in water and treated with magnesium carbonate. (The magnesium salt of azelaic acid is much less soluble in water than that of suberic acid.) The most insoluble fraction of magnesium salt was treated with dilute hydrochloric acid, and the free dibasic acid extracted with ether. The acid obtained in this way melted at 139°, so that more than traces of azelaic acid could not have been present.†

(c) *Isolation of monobasic acid formed.* The aqueous distillate containing the liquid fatty acid was extracted with petroleum (b. p. 40—60°), and the solution dried with sodium sulphate. The liquid left after recovering solvent was freed from traces of petroleum by gently warming under reduced pressure and on cooling to 9° the acid solidified in colourless laminæ, m. p. 14°; the yield of monobasic acid was 1·4 g. (Theory for octoic acid is 2·05 g.) In conjunction with the results mentioned in the footnote,‡ these observations show that the greater part of the monobasic acid was octoic acid.

(d) *Estimation of oxalic acid formed.* The calcium oxalate precipi-

* The light petroleum washings from unchanged dihydroxystearic acid were reserved and added to the ethereal solution of oxidation products.

† In another experiment, the dibasic acid (6·5 g.) obtained from a larger quantity of dihydroxystearic acid was examined according to the above method and no azelaic acid was detected.

‡ In another experiment, starting from 16 g. of dihydroxystearic acid, 4·75 g. of fluid fatty acid distilled steadily at 233—235° at ordinary pressure. (Octoic acid boils at 236–237° and nonoic acid at 253–254°.) The equivalent found was 142·2; $C_8H_{16}O_2$ requires 144·0.

tated from the aqueous liquor from (c), made alkaline with ammonia, by the addition of calcium sulphate solution, was collected after 12 hours and treated with warm acetic acid. The residue was washed with water, and the oxalic acid estimated by titration with 1% potassium permanganate at 60° (Found : 0·86 g. ; calc., 1·28 g.). This quantitative result is, however, not offered with the same degree of confidence as those for octoic and suberic acids.

Oxidation of Dihydroxystearic Acid by Edmed's Method.—To a hot solution of dihydroxystearic acid (6·0 g.) in 150 c.c. of 1% caustic potash, 8·2 g. of potassium permanganate dissolved in 450 c.c. of water were added and oxidation was continued until the potassium manganate first formed was completely reduced (about 10 minutes). Manganese dioxide was filtered off, the filtrate acidified with sulphuric acid, and unchanged dihydroxystearic acid (3·0 g.) was filtered off. The oxidation products were isolated from the filtrate as in the above experiments.

The extracted dibasic acid (1·3 g.) was treated with cold ether, and the more soluble fraction (0·9 g.) converted into magnesium salt as in 1 (b) above. The most insoluble fraction of the latter yielded almost pure azelaic acid (m. p. 105°) (Equivalent found, 93·8; required, 94·0).

The fraction of dibasic acid less soluble in ether melted at 137—138° and had the equivalent 87·5. It was therefore mainly suberic acid.

Conclusions.—(1) The oxidation of dihydroxystearic acid by the method described in 1 (a) therefore leads to the formation of : suberic acid, in amount at least 80% of the theoretical; octoic acid, in amount at least 70% of the theoretical; and oxalic acid.

(2) By Edmed's original method, both suberic and azelaic acid are formed.

This work was carried out in continuation of researches begun under the auspices of the Food Investigation Board of the Department of Scientific and Industrial Research.

A grant from the Department of Scientific and Industrial Research to one of us (E. N. M.) rendered it possible for him to take part in the research and is gratefully acknowledged.

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CCLXVIII.—*The Effect of Ultra-violet Light on Dried Hydrogen and Oxygen.*

By Herbert Brereton Baker and Margaret Carlton.

In 1922 Coehn and Tramm (*Ber.*, **56**, 455), working with an "electrolytic" mixture of hydrogen and oxygen, found that the gases interacted at the same rate when exposed to the light from a quartz mercury lamp whether they were dry or moist. This conclusion, if confirmed, would have an important bearing on the theory of the determining effect of water vapour. It was thought necessary to repeat the experiments, since these authors had not succeeded in attaining the same degree of resistance to the effect of heat on the dried gases as had been attained by one of us (Baker, J., 1902, **81**, 400). In these experiments, it was shown that the highly dried, "pure" gas mixture could be heated to redness and a silver wire melted in it without measurable action. Coehn and Tramm have succeeded in obtaining the gases so pure and dry that no explosion took place on heating to redness, but slow combination only. It is impossible to say why their gases did not give the same results as those described in 1902. Their work, as described, seems to have been most carefully carried out. The only point in their apparatus to which objection might be taken is the presence of two greased taps. The interaction of hydrogen and oxygen is one of those most susceptible to the slightest trace of impurity; it is possible that a few molecules of vapour from the lubricant used may have produced a diminution in the resistance to chemical action.

In our experiments the gases were produced by the electrolysis of a solution of barium hydroxide which had been recrystallised fifteen times. The reaction tubes were of the clearest fused quartz bent into L shape. The shorter arm was closed. The tubes were boiled in a mixture of chromic and nitric acids; after washing with distilled water, they were roughly dried in an electric oven and heated to bright redness after being exhausted. Air dried by phosphorus pentoxide was admitted after heating, the process being repeated six times.

The tubes were then filled with highly purified and dried mercury and the gaseous mixture was admitted over a mercury trough. It had been found, in the previous work, that the gases evolved during the electrolysis were not as resistant to chemical action in the first as in the later stages. The gaseous mixture was therefore allowed to escape during 3 days before being collected in the quartz tubes. Pairs of tubes, similar in diameter and in shape,

were filled at the same time. Into one of the pair was introduced a plug of phosphorus pentoxide which had been distilled in oxygen, the other being left in the undried condition. Both tubes, mounted on a special stand, were left in the dark room during the time specified.

The pair of tubes was then arranged symmetrically near a quartz mercury vapour lamp, so that both were exposed, as nearly as possible, to the same radiation. The part of the tube containing the phosphorus pentoxide was shielded from the direct rays of the lamp. The amount of chemical action was estimated by measurement of the rise of the mercury column in each tube, the temperature and pressure being noted at the same time.

In all, six pairs of tubes have been tested, prepared in the same way but with different lengths of time allowed for drying. In every case, there was a marked difference between the wet and the dry tubes, the latter showing in some cases no measurable action.

The following table is a summary of the results.

	Period of drying.	Time of exposure to light (hours).	Rise in mercury column (mm.). Dry.	Wet.
1	2 weeks	7	4	14
2	3 weeks	5	4	30
	After 12 hours' interval	6	9	43
3	4 weeks	5	0	6·1
	After 12 hours' interval	3	1	4·5
	After 12 hours' interval	5	6·5	7·2
4	7 weeks	6¼	0	2·3
	After 12 hours' interval	6½	0·35	6·5
5	8 weeks	5	0·5	5
	After 12 hours' interval	5	0·1	5
6	8 weeks	5	0	6·1
	After 12 hours' interval	6	0	6·2
	After 12 hours' interval	9	0·5	9·1
	After 12 hours' interval	8½	1·5	10
	After 12 hours' interval	6	10	12·5

Note, added August 1st.—One tube, dried for 12 weeks, was exposed at a distance of 2 cm. from the quartz mercury lamp for 13 hours without showing any measurable contraction.

It should be noticed that during the 12-hour intervals renewed drying is taking place, so that it is probable that only a fraction of the water produced (if any) during a day's exposure is available for promoting the chemical action on the next day.

It is also noticeable that in experiments 3 and 6 there is a sudden rise in the amount of gas combined in the dry tubes. This seems to be due to the amount of water formed during the previous day being too great to be absorbed by the drying agent during the night, so that the gases start in a comparatively moist condition.

It was found impracticable to leave the lamp running all night,

as it had a tendency, after some hours' run, to go out. On two occasions it was found that an exposure of 5 hours to the light had produced no action in either the wet or the dry tube. On examination it was found that a purple film had formed on the inside of the quartz tube of the lamp. Professor R. Wood (*Proc. Roy. Soc.*, 1924, *A*, 688) noticed the same phenomenon and he recommended the opening of the tube and the polishing of the interior with rouge. We found, however, that the full activity of the lamp could be restored by strongly heating the quartz tube of the lamp with a hot bunsen burner.

It was noteworthy that, in none of the tubes, wet or dry, was any tailing of the mercury observed; ozone therefore was not formed. The loss of mobility of mercury exposed to ozone forms one of the most delicate tests known. In two cases, both of wet tubes, a yellow film was formed. This proved to be mercuric oxide and amounted in the one tube in which it was determined to 4·1 mg. Its formation could not have been due to ozone, which produces mercurous oxide, never mercuric oxide.

Professor Bone (private communication) considers that phosphorus pentoxide cannot exert its full drying power when its temperature is allowed to rise above 25°. In the experiments described above, the gases generally reach a temperature of above 30°. In two of them the part of the tube containing the pentoxide was kept surrounded by ice during the whole of the run. The rate of union was not found to be altered by this treatment.

We wish to express our thanks to Messrs. Brunner Mond and Co. for a grant for the purchase of apparatus.

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CCLXIX.—*Imino-aryl Ethers. Part III. The Molecular Rearrangement of N-Phenylbenziminophenyl Ether.*

By ARTHUR WILLIAM CHAPMAN.

IT is on record (Mumm, Hesse, and Volquartz, *Ber.*, 1915, **48**, 379) that benzoyldiphenylamine (II) may be obtained by heating *N*-phenylbenziminophenyl ether (I) at 240° for 1 hour.

$$\text{(I.)}\quad \text{PhO·CPh:NPh} \xrightarrow{\text{heat}} \text{O:CPh·NPh}_2 \quad \text{(II.)}$$

On repeating this experiment, unchanged material only could be recovered. However, benzoyldiphenylamine was obtained

after heating at 270—300° for 2 hours. The transformation had apparently occurred completely and without the formation of by-products, and therefore merited further investigation, especially as no quantitative study seems to have been made of any of the isomeric changes among imino-ethers of the aliphatic series and imino-esters (Pinner, "Die Imidoaether," 1892; Wislicenus and Goldschmidt, *Ber.*, 1900, **33**, 1470; Lander, J., 1903, **83**, 406; Wheeler and Johnson, *Amer. Chem. J.*, 1903, **30**, 24; Busch, Blume, and Pungs, *J. pr. Chem.*, 1909, **79**, 513; Kuhara, *Cent.*, 1911, I, 1514; Short and Smith, J., 1922, **121**, 1803).

The dynamics of the reaction were first studied. The purified imino-ether was heated in a thermostat maintained at various temperatures between 220° and 300°, and the product was submitted to thermal analysis (Hollemann, "Direkte Einfuhrung von Substituenten in den Benzolkern," 1910, p. 26). The freezing-point curve of mixtures of the two components was drawn from the following observations on mixtures of *N*-phenylbenziminophenyl ether with known quantities (*a*) of benzoyldiphenylamine.

a%	20	30	40	50	60	70	80	90	95	100
F. p.	107·8°	123·8°	134·8°	144·8°	152·7°	159·7°	165·6°	171·6°	174·6°	176·7°

The freezing points of mixtures containing less than 20% of benzoyldiphenylamine could not be determined accurately.

The progress of the transformation agreed closely with that required by the unimolecular formula; a typical series of observations is the following, t being the time of heating in minutes, x the percentage of benzoyldiphenylamine formed, and the temperature 262°:

t	32	60	120	181	240	300	360	
x	33	54	80	90	94	98	99·5	
$k \times 10^3$	5·4	5·6	5·8	5·5	5·1	5·7	5·6	Mean 5·5

The velocity coefficients at different temperatures are:

Temp.	228°	246—247°	262°	272°	278°	282°	287—288°	292—293°
$k \times 10^3$	0·1—0·2	1·6	5·5	11	18	23	34	45

The mean temperature coefficient between 246° and 292° was 2·06 per 10°.

N-Phenylbenzimino-*o*-chlorophenyl ether and *N*-phenylbenzimino-*p*-chlorophenyl ether, heated at 270—290° for 2 hours, gave benzoyl-*o*- and -*p*-chlorodiphenylamine, respectively, by changes corresponding to that of (I) into (II).

The mobile group must therefore have become attached to the nitrogen atom by the nuclear carbon atom originally attached to the oxygen (compare Montagne, *Ber.*, 1918, **51**, 1479).

The assumption has frequently been made that in changes of this character the migration of the mobile atom or group is preceded by its partial dissociation from the remainder of the molecule, followed by a redistribution of the valency bonds and recombination to form the isomeric compound; some workers have assumed complete dissociation (Brühl, *Ber.*, 1899, **32**, 2326; Lapworth, J., 1901, **79**, 1265; Nef, *J. Amer. Chem. Soc.*, 1904, **26**, 1549). The absence of by-products formed by the combination of two similar free radicals could be accounted for by regarding the dissociation as ionic in character. Recently Meerwein and van Emster (*Ber.*, 1922, **55**, 2500; compare also *Annalen*, 1923, **435**, 190, 207) have applied this view to the interpretation of the isomeric change of camphene hydrochloride into bornyl chloride, and have shown that the velocities of the transformation in different solvents are proportional to the ionising powers of the latter. Others, however, have preferred to express the course of such transformations in terms of partial valencies without assuming the formation of ions or free radicals (Robinson, *Mem. Manc. Lit. Phil. Soc.*, 1920, **64**, No. 4; Tiffeneau, *Rev. Gen. Sci.*, 1907, 583; Stark, "Prinzipien der Atomdynamik," 1915, III, 156; Mumm, Hesse, and Volquartz, *loc. cit.*).

It seemed desirable to test the validity of the ionic hypothesis in the present instance, and a number of measurements were made of the electrical conductivity of the imino-ether and its isomeride before, during, and after the completion of the isomeric change. The results obtained were mainly comparative. The specific conductivity of the imino-ether between 250° and 280° was of the order 10^{-8} to 10^{-9}. The low conductivity of the imino-ether remained constant so long as no appreciable isomeric change occurred, as was shown by heating the ether at 200° for several hours. When the imino-ether was heated at a higher temperature, an increase in conductivity occurred simultaneously with the isomeric change. At first rapid, it became slower, and finally the conductivity remained constant, the end of the increase coinciding with the completion of the isomeric change. Samples of benzoyldiphenylamine had identical conductivities within the range of experimental error whether prepared (*a*) by heating the imino-ether, or (*b*) as in (*a*) but subsequently crystallised from alcohol and dried, or (*c*) from diphenylamine and benzoyl chloride. The specific conductivity was of the order of 10^{-6} to 10^{-7} at 250—280°.

These observations can readily be explained in terms of the ionic hypothesis by supposing that the first stage consists in the rupture of the bond between the phenyl radical and the oxygen atom, a phenyl ion and an ionised residue being produced; re-

arrangement of the linkings in the residue follows, and combination of the phenyl ion with the nitrogen atom :

$$\mathrm{PhC}\lessdot^{\mathrm{NPh}}_{\mathrm{OPh}} \longrightarrow \mathrm{PhC}\lessdot^{\mathrm{NPh}}_{\mathrm{O}\cdots} + \mathrm{Ph}\cdots \longrightarrow$$

$$\mathrm{PhC}\lessdot^{\mathrm{NPh}\cdots}_{\mathrm{O}} + \mathrm{Ph}\cdots \rightleftharpoons \mathrm{PhC}\lessdot^{\mathrm{NPh}_2}_{\mathrm{O}}.$$

The first stage would give the reaction its unimolecular character, the succeeding ones being comparatively very rapid. The final stage would result in an equilibrium between ionised and non-ionised benzoyldiphenylamine.

The results of the determinations with different samples of benzoyldiphenylamine rendered it unlikely that the observed conductivity change was due to a trace of a by-product formed during the transformation; but the possibility was not excluded that it might arise from the constant presence of a trace of impurity in the changing medium of the molten mixture. Such a source of error—which might arise from the liberation of water adsorbed on the glass walls of the cell, as well as from the presence of impurities in the substances used—could be guarded against only partially by careful purification of material and apparatus, and hence it was decided to employ a more trustworthy test of the ionisation of the materials undergoing change.

N-*p*-Tolylbenzimino-*p*-tolyl ether undergoes rearrangement at the same temperatures as *N*-phenylbenziminophenyl ether. If the change is ionic in the one case, it should be so in the other, and if a mixture of these two imino-ethers were heated at the transformation temperature a certain amount of benzoylphenyl-*p*-tolylamine should be formed by exchange of the mobile groups, in addition to the two symmetrical products.

$$\mathrm{PhC(:NPh)\cdot OPh} \longrightarrow \mathrm{PhCO\cdot NPh}\cdots + \mathrm{Ph}\cdots \rightleftharpoons \mathrm{PhCO\cdot NPh_2}$$

$$\rightleftharpoons \mathrm{PhCO\cdot NPh(C_7H_7)}$$

$$\mathrm{PhC(:N\cdot C_7H_7)\cdot O\cdot C_7H_7} \rightarrow \mathrm{PhCO\cdot N\cdot C_7H_7}\cdots + \mathrm{C_7H_7}\cdots \rightleftharpoons \mathrm{PhCO\cdot N(C_7H_7)_2}$$

A mixture of *N*-phenylbenziminophenyl ether and *N*-*p*-tolylbenzimino-*p*-tolyl ether in equal molecular proportions was heated at 290° until the freezing point of the product was constant (139·8°). This freezing point was identical with that of a freshly made mixture of benzoyldiphenylamine and benzoyldi-*p*-tolylamine in equal molecular proportions. After the latter mixture had been heated for several hours at 250—290°, the freezing point was unchanged, showing that here again no third substance was produced. Inter-

change of groups to form benzoylphenyl-*p*-tolylamine had therefore not taken place.

The conclusion cannot be resisted, in view of this evidence, that the isomeric change of an imino-ether into a substituted amide is not ionic in character. This conclusion can probably be extended to other isomeric changes, where, under the influence of heat, an aryl group migrates to a different position in the molecule, and serves to confirm the view, recently expressed (*Ann. Rep.*, 1924, 98), that the ionic hypothesis should be applied only to those structures which exhibit independent evidence of capacity to ionise.

Experimental.

Preparation and Purification of Materials.—The *N*-phenylbenziminophenyl ether was prepared by the same method as *N*-phenylbenzimino-*m*-hydroxyphenyl ether (J., 1922, **121**, 1679). It was recrystallised from alcohol until both the m. p. (105°) and the velocity of isomeric change were constant. Further recrystallisation from benzene produced no effect on either property.

The benzoyldiphenylamine prepared from diphenylamine and benzoyl chloride was recrystallised from alcohol until the m. p. was constant.

Dynamical Experiments.—Five grams of imino-ether were used for each determination. The material, in a test-tube, was rapidly heated to approximately the required temperature in a separate oil-bath and then quickly transferred to an electrically heated, oil-filled thermostat maintained within 0·5° of the temperature of the experiment. At the end of the required time the tube was removed; the cooled melt could then be analysed at leisure.

The freezing-point determinations were conducted in the same tube, which was enclosed in a wider tube, itself immersed in an oil-bath maintained a few degrees below the freezing point of the mixture. Readings were easily obtained concordant to 0·25°, corresponding to an accuracy of 0·5%.

The freedom of the benzoyldiphenylamine from impurity when obtained by prolonged heating of the imino-ether (10 g., heated at 280° for 3 hours and then at 290° for 50 minutes) was proved by the identity of its freezing point with that of pure benzoyldiphenylamine (176·7°). A special thermometer was used which could be read to 0·05°.

Isomeric Change of Chloro-substituted Imino-ethers.—These compounds were prepared from *o*- and *p*-chlorophenols by the method referred to above.

N-*Phenylbenzimino*-o-*chlorophenyl ether* crystallises from alcohol in almost colourless, stout prisms, m. p. 88°. It is very soluble in hot

alcohol, but only sparingly soluble in cold (Found: N, 4·6. $C_{19}H_{14}ONCl$ requires N, 4·55%).

When heated at 270—280° for 1 hour and then crystallised from alcohol, it yielded hard crusts of constant m. p. 95—96°, which did not depress the m. p. of benzoyl-*o*-chlorodiphenylamine prepared as described below (Found: N, 4·7. $C_{19}H_{14}ONCl$ requires N, 4·55%).

N-*Phenylbenzimino*-p-*chlorophenyl ether* crystallised from alcohol in pale yellow, long prisms, m. p. 92—93° (Found: N, 4·75%). Hydrolysis with 50% sulphuric acid yielded *p*-chlorophenyl benzoate (m. p. 88—88·5°) identical with a sample prepared from *p*-chlorophenol. When heated at 280—290° for 2 hours and then recrystallised from alcohol, it yielded long prisms of constant m. p. 109—110° which did not depress the m. p. of benzoyl-*p*-chlorodiphenylamine prepared as described below (Found: N, 4·7%).

Benzoyl-o-, -m-, and -p-*chlorodiphenylamines* were prepared as described by Ullmann (*Annalen*, 1907, **355**, 338) by heating the corresponding chlorophenylanthranilic acids. o-*Chlorodiphenylamine* was obtained only after heating *o*-chlorophenylanthranilic acid at 300—320° for 5 hours. It is a pale yellow oil, b. p. 300—303°/753 mm.

The bases were benzoylated by heating with benzoyl chloride, and the benzoyl derivatives crystallised from alcohol.

Benzoyl-o-*chlorodiphenylamine*, m. p. 95° (Found: N, 4·6%), and *benzoyl*-m-*chlorodiphenylamine*, m. p. 101—102° (Found: N, 4·6%), crystallise in hard crusts; the m. p. of the latter was depressed by the addition of either of the substances prepared by heating the *o*- and *p*-chloro-iminoethers. *Benzoyl*-p-*chlorodiphenylamine* crystallises in prisms, m. p. 109—109·5° (Found: N, 4·7%).

Measurements of Electrical Conductivity.—The electrodes were bright platinum foil cylinders 1·0 and 0·7 cm. respectively in diameter and 1 cm. high, secured in position one inside the other by sealing their platinum stems through two rigidly connected glass tubes. The constant of the cell was approximately $2·4 \times 10^{-2}$ at 21°, and no appreciable leak could be detected at 275°.

As the resistances to be measured were very high (10^5 to 10^7 ohms), the arrangement devised by Ambronn (*Ann. Physik*, 1919, **58**, 139) was employed, consisting of a battery and galvanometer connected to the conductivity cell through a rotating commutator which reversed the current through the cell about 100 times per second. The apparatus was calibrated by comparison with a series of standard high resistances.

The samples (5 g. in each case) were well dried and heated as in the dynamical experiments. The electrodes were immersed in the

fused material, and readings taken from time to time throughout the whole period of the transformation. The temperatures employed varied from 260° to 280°.

N-p-*Tolylbenzimino*-p-*tolyl ether*, prepared from benz-*p*-toluidide-iminochloride and *p*-cresol by the method already described, formed very pale yellow prisms, m. p. 65—66° (Found : N, 4·75. $C_{21}H_{19}ON$ requires N, 4·65%). When heated at 270—300° for 2 hours, it yielded *benzoyldi*-p-*tolylamine ;* this, prepared also from di-*p*-tolylamine and benzoyl chloride, formed nearly colourless prisms, m. p. 124—125° (Found : N, 4·7. $C_{21}H_{19}ON$ requires N, 4·65%).

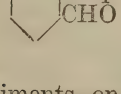
The author wishes to express his indebtedness to the Chemical Society for a grant which has defrayed part of the expenses of this investigation, and to Messrs. Metropolitan-Vickers Electrical Company, Ltd., for the loan of the rotating commutator.

The University, Sheffield. [*Received, June 20th,* 1925.]

CCLXX.—*Substitution in Derivatives of Quinol Ethers.*

By Leon Rubenstein.

The investigation of substitution in the case of dialkyloxy vicinal benzene derivatives of type I (Davies and Rubenstein, J., 1923, **123**, 2830) showed that during nitration each alkyloxy-group OR,OR_1 exerts its para-directing influence independently of the other, whereas during bromination only the group –OR is potent in determining the orientation of the brominated product. The relative amounts of the isomerides produced in the nitration experiments, which could not then be estimated, have now been determined in the case of *o*-veratraldehyde (Perkin, Robinson, and Stoyle, J., 1924, **125**, 2355). The results obtained in those investigations made it desirable to examine the nitration and bromination of substances of type II in which only ortho-substitution with respect to the alkyloxy-groups can take place.

(I.) 



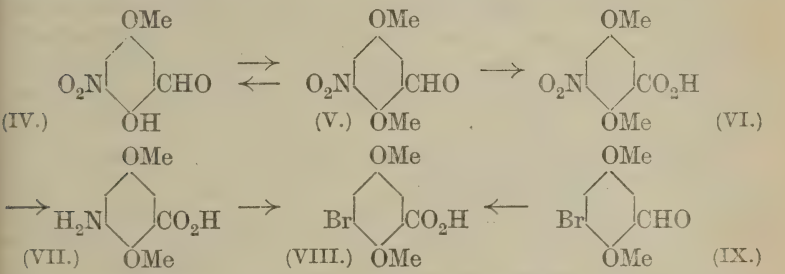
(II.)



(III.)

Experiments on the nitration of 2-hydroxy-5-methoxybenzaldehyde (III) indicate that the substance formed is the 3-nitro-benzaldehyde (IV), for when its methylation product (V) is hydrolysed 3-*nitro*-2-*hydroxy*-5-*methoxybenzaldehyde* is reformed. The bromin-

ation of 2-hydroxy-5-methoxybenzaldehyde yields the 3-bromobenzaldehyde, as is shown in the following manner: 3-*Nitro*-2 : 5-*dimethoxybenzaldehyde* (V) is oxidised to 3-*nitro*-2 : 5-*dimethoxybenzoic acid* (VI), which is reduced to 3-*amino*-2 : 5-*dimethoxybenzoic acid* (VII); from this by the Sandmeyer process is produced 3-*bromo*-2 : 5-*dimethoxybenzoic acid* (VIII), identical with the acid obtained by oxidising bromo-2-hydroxy-5-methoxybenzaldehyde after methylation (IX).



The nitration of 2 : 5-dimethoxybenzaldehyde gives a mixture of 6-*nitro*-2 : 5-*dimethoxybenzaldehyde* (80%) and 3-*nitro*-2 : 5-*dimethoxybenzaldehyde* (20%). The former substance has its nitro-group in the ortho-position with respect to the aldehyde group, for it gives an indigotin derivative when treated with acetone and alkali. It yields 6-nitro-2 : 5-dimethoxybenzoic acid on oxidation. The bromination of 2 : 5-dimethoxybenzaldehyde gives 6-*bromo*-2 : 5-*dimethoxybenzaldehyde* as the only product, and from this 6-*bromo*-2 : 5-*dimethoxybenzoic acid* is obtained by oxidation.

The remaining portion of the work consists in the investigation of the nitration and the bromination of 2 : 5-dimethoxyacetanilide. The nitration of this substance yields 4-*nitro*-2 : 5-*dimethoxyacetanilide*, as is shown by the fact that hydrolysis converts it into the nitro-2 : 5-dimethoxyaniline which on diazotisation and subsequent treatment in the Sandmeyer manner yields 3-*bromo*-6-*nitroquinol dimethyl ether*. On bromination, 2 : 5-dimethoxyacetanilide yields 4-*bromo*-2 : 5-*dimethoxyacetanilide*, the usual proof being applied, namely, conversion into the 4-*bromo*-2 : 5-*dimethoxyaniline*, diazotisation, and treatment with cuprous bromide to give dibromoquinol dimethyl ether.

Experimental.

2-Hydroxy-5-methoxybenzaldehyde was obtained by Tiemann and Müller (*Ber.*, 1881, **14**, 1990) in small yield, but the following modification gives much better results. Quinol monomethyl ether (40 g.) dissolved in a concentrated aqueous solution of sodium hydroxide (19 g. in 55 c.c. of water) is heated on a water-bath

while chloroform (42 g.) and sodium hydroxide solution (56 g. in 60 c.c. of water) are added alternately during 2 hours. The mixture is then heated for 1 hour, the sodium salt of the aldehyde separating in yellow, metallic crystals. The whole is strongly acidified, steam-distilled, the distillate extracted with ether, and the ethereal extract kept for some time over a concentrated solution of sodium bisulphite. The major portion of the ether is distilled off and the bisulphite compound of the aldehyde, which separates, is removed, decomposed by hot dilute sulphuric acid, and the aldehyde extracted with ether. The ether is removed and the residue distilled under reduced pressure, when 2-hydroxy-5-methoxybenzaldehyde is obtained as a light yellow, refracting liquid, b. p. 124°/12 mm. (yield 8·5 g., *i.e.*, 25%).

3-*Nitro*-2-*hydroxy*-5-*methoxybenzaldehyde*.—To a cold solution of 2-hydroxy-5-methoxybenzaldehyde (10 g.) in glacial acetic acid (50 c.c.) is added with cooling and stirring a solution of nitric acid (50 c.c.; *d* 1·42) in glacial acetic acid (50 c.c.), the temperature being maintained between 10° and 20°. 3-Nitro-2-hydroxy-5-methoxybenzaldehyde, which soon begins to separate, is collected after a few hours (yield 6·5 g.; m. p. 127°). The glacial acetic acid solution is diluted with water, neutralised with sodium bicarbonate, and extracted with ether; from the extract a further 4·5 g. of the substance is obtained (total yield 88%). 3-Nitro-2-hydroxy-5-methoxybenzaldehyde crystallises in bright yellow needles, m. p. 132°. It does not yield an indigotin derivative when treated with acetone and sodium hydroxide solution. With ferric chloride solution, it gives a red coloration (Found: N, 7·2. $C_8H_7O_5N$ requires N, 7·1%).

The p-*nitrophenylhydrazone* crystallises in scarlet prisms, decomp. 250°.

3-*Nitro*-2 : 5-*dimethoxybenzaldehyde*.—A solution of 3-nitro-2-hydroxy-5-methoxybenzaldehyde (6 g.) in dry chloroform (20 c.c.) and methyl iodide (10 c.c.) is heated on a water-bath while finely powdered silver oxide (6 g.) is added during 2 hours. After being heated for a further 1 hour, the mixture is filtered hot, some of the chloroform evaporated, and the solution cooled; 3-nitro-2 : 5-dimethoxybenzaldehyde then crystallises in pale yellow needles, m. p. 113°. More of the substance is obtained from the mother-liquors (yield almost theoretical) (Found: N, 6·85. $C_9H_9O_5N$ requires N, 6·7%). When it is boiled for a short time with 10% sodium hydroxide, and the solution is acidified, 3-nitro-2-hydroxy-5-methoxybenzaldehyde can be extracted from the precipitate obtained.

3-*Bromo*-2-*hydroxy*-5-*methoxybenzaldehyde*.—2-Hydroxy-5-meth-

oxybenzaldehyde (6 g.) is dissolved in glacial acetic acid (30 c.c.), and powdered, freshly-fused sodium acetate (3·6 g.) added. The suspension is well stirred, cooled to 5°, and treated with a solution of bromine (6 g.) in glacial acetic acid (12 c.c.), when 3-*bromo*-2-*hydroxy*-5-*methoxybenzaldehyde* rapidly separates. After remaining for a few hours, the mixture is diluted with water and the solid collected (yield 7·3 g. or 80%). It crystallises from aqueous alcohol in light brown needles, m. p. 107° (Found : Br, 35·0. $C_8H_7O_3Br$ requires Br, 34·6%). The p-*nitrophenylhydrazone* forms scarlet prisms, decomp. above 250°.

3-*Bromo*-2 : 5-*dimethoxybenzaldehyde*.—A solution of 3-bromo-2-hydroxy-5-methoxybenzaldehyde (6·5 g.) in alcohol (59 c.c.) is boiled under reflux during the gradual addition of methyl *p*-toluenesulphonate (10·5 g.) and 30% sodium hydroxide solution (4 c.c.). After boiling for 3 hours, the red alcoholic solution is diluted with water and the solid collected; after twice crystallising from aqueous alcohol, it forms needles, m. p. 63° (Found : Br, 32·3. $C_9H_9O_3Br$ requires Br, 32·6%).

Nitration of 2 : 5-*Dimethoxybenzaldehyde*.—Finely-powdered 2 : 5-dimethoxybenzaldehyde (3 g.) was added with cooling and stirring to cold nitric acid (12 c.c.; *d* 1·42). After remaining at room temperature for several hours, the mixture was diluted with water, and the solid (3·4 g.) collected. The mixture, m. p. 130—153°, was fractionally crystallised from alcohol, the main product being 6-*nitro*-2 : 5-*dimethoxybenzaldehyde* (*vide ante*), m. p. 159°. The mother-liquors deposited a small amount of 3-*nitro*-2 : 5-*dimethoxybenzaldehyde* (m. p. 113°), which gave no depression of melting point when mixed with a sample of 3-nitro-2 : 5-dimethoxybenzaldehyde prepared by the methylation of 3-nitro-2-hydroxy-5-methoxybenzaldehyde (p. 2000).

6-Nitro-2 : 5-dimethoxybenzaldehyde crystallises from alcohol in pale yellow needles, m. p. 159° (Found : N, 6·8. $C_9H_9O_5N$ requires N, 6·7%). The p-*nitrophenylhydrazone* forms scarlet prisms, m. p. 245—250° (decomp.).

6-*Bromo*-2 : 5-*dimethoxybenzaldehyde*.—A cooled solution of 2 : 5-dimethoxybenzaldehyde (2·8 g.) in glacial acetic acid (16 c.c.) is treated with bromine (2·8 g.) in glacial acetic acid (8 c.c.), kept for 2 days, and diluted with water; an oil then separates which rapidly solidifies. It crystallises from alcohol in pale grey needles, m. p. 125—126°, which become pink on exposure to the air (Found : Br, 29·1. $C_9H_9O_3Br$ requires Br, 28·7%). The p-*nitrophenylhydrazone* consists of hexagonal, scarlet prisms, m. p. 204—206°.

3-*Nitro*-2 : 5-*dimethoxybenzoic Acid*.—3-Nitro-2 : 5-dimethoxybenzaldehyde (6 g.) is added to water (60 c.c.) containing potassium

bicarbonate (4·2 g.), and boiled during the addition of potassium permanganate solution (6 g. in 60 c.c. of water). The hot solution is filtered, allowed to cool, and unchanged aldehyde collected. The reddish-yellow aqueous solution is acidified with dilute hydrochloric acid, when 3-nitro-2 : 5-dimethoxybenzoic acid (3·5 g.) is precipitated. It crystallises from hot water in long needles, m. p. 182—183° (Equiv. : found, 225; calc., 227).

6-*Nitro*-2 : 5-*dimethoxybenzoic Acid.* — 6-Nitro-2 : 5-dimethoxybenzaldehyde is oxidised as described above. The acid crystallises from hot water in pale yellow prisms, m. p. 192° (Equiv. : found, 229; calc., 227).

3-*Amino*-2 : 5-*dimethoxybenzoic Acid.*—A mixture of 3-nitro-2 : 5-dimethoxybenzoic acid (7 g.) and concentrated hydrochloric acid (24 c.c.) is gradually treated with tin (7 g.) and heated on a water-bath for 3 hours, water (50 c.c.) is added, and the tin removed from the hot solution as sulphide. The colourless filtrate is evaporated under reduced pressure, when the *hydrochloride* of 3-*amino*-2 : 5-*dimethoxybenzoic acid* separates in long, white needles (yield 5 g. or 80%).

The hydrochloride is easily soluble in water or alcohol, more difficultly soluble in concentrated hydrochloric acid, from which it can be crystallised. The solutions turn pink and then red on exposure to the air. When heated, the solid becomes very dark at 170° and decomposes at 215°. 3-*Amino*-2 : 5-*dimethoxybenzoic acid* is obtained by treating a solution of the hydrochloride in a small quantity of water with solid sodium carbonate until it is just acid to Congo-red, and evaporating under reduced pressure; after a long time, the acid separates in white, slender needles which turn black at 170° and decompose at 210—215°. It is soluble in acids, alkalis, and hot water; the latter two solutions turn green on exposure to the air (Found : N, 6·9. $C_9H_{12}O_4N$ requires N, 7·0%).

3-*Bromo*-2 : 5-*dimethoxybenzoic Acid.*—A mixture of 3-bromo-2 : 5-dimethoxybenzaldehyde (5·5 g.), water (55 c.c.), and potassium bicarbonate (3·8 g.) is boiled during the addition of 10% potassium permanganate (55 c.c.), filtered hot, cooled, and again filtered. The colourless filtrate is acidified with dilute hydrochloric acid, and the precipitated 3-*bromo*-2 : 5-*dimethoxybenzoic acid* (yield 4·5 g. or 85%) is crystallised from aqueous alcohol, when it is obtained in white, microscopic prisms, m. p. 132° (Equiv. : found, 258; calc., 261).

6-*Bromo*-2 : 5-*dimethoxybenzoic Acid.*—6-Bromo-2 : 5-dimethoxybenzaldehyde is oxidised as described above. The acid crystallises from aqueous alcohol in white, microscopic prisms, m. p. 164—165° (Equiv. : found, 259; calc., 261).

4 : 4′ : 7 : 7′-*Tetramethoxyindigotin*.—Aqueous potash (1 c.c. of 10%) is added to a solution of 6-nitro-2 : 5-dimethoxybenzaldehyde (0·4 g.) in acetone (2 c.c.). The deep blue liquid is mixed with water (20 c.c.) and boiled for a few minutes; the indigotin then separates. It has a rich deep blue appearance and crystallises from nitrobenzene in deep purple rhombs which sublime at 350°.

4-*Bromo*-2 : 5-*dimethoxyacetanilide*.—When 2 : 5-dimethoxyacetanilide (5 g.) dissolved in glacial acetic acid (25 c.c.) is treated with bromine (3·3 g.) in 4 c.c. of glacial acetic acid, 4-*bromo*-2 : 5-*dimethoxyacetanilide* soon separates from the well-cooled solution. After the mixture has been diluted with water, and the acetic acid neutralised with sodium carbonate, ether extracts the product, which crystallises from dilute alcohol in pale pink rhombs, m. p. 122° (yield 5·6 g. or 80%) (Found: Br, 29·3. $C_{10}H_{12}O_3NBr$ requires Br, 29·1%).

4-*Bromo*-2 : 5-*dimethoxyaniline Hydrochloride*.—4-Bromo-2 : 5-dimethoxyacetanilide (12 g.) is boiled with 20% alcoholic hydrochloric acid (20 c.c.) for 15 minutes; the 4-*bromo*-2 : 5-*dimethoxyaniline hydrochloride* which separates crystallises from alcohol in white, microscopic plates which become blue at 160° and decompose above 300°.

4-*Bromo*-2 : 5-*dimethoxyaniline* forms pale pink prisms, m. p. 106°. The *hydrobromide* is obtained by keeping an ethereal solution of the base in contact with hydrobromic acid (*d* 1·5), when it slowly separates in fine, yellow needles which turn blue at 160° and decompose slowly above this temperature.

Diazotisation. Methyl nitrite is passed through a solution of 4-bromo-2 : 5-dimethoxyaniline hydrobromide (20 g.) in glacial acetic acid (60 c.c.) at 10°. The deep brown solution of 4-bromo-2 : 5-dimethoxybenzenediazonium bromide is poured into dry ether, the ether decanted off, and the solid diazonium salt dissolved in ice-cold water (40 c.c.). The aqueous solution is added cautiously to a solution of cuprous bromide in concentrated hydrobromic acid and heated on a water-bath; nitrogen is then evolved and 2 : 5-dibromoquinol dimethyl ether separates. This crystallises from alcohol in colourless needles, m. p. 143°, not depressed on admixture with the dibromoquinol dimethyl ether prepared by the bromination of quinol dimethyl ether.

4-*Nitro*-2 : 5-*dimethoxyacetanilide*.—A solution of 2 : 5-dimethoxyacetanilide (10 g.) in glacial acetic acid (50 c.c.) is treated at 5° with nitric acid (*d* 1·42; 10 c.c. in 50 c.c. of glacial acetic acid). After 1 hour, water is added. The 4-*nitro*-2 : 5-*dimethoxyacetanilide* which separates (yield 11 g. or 90%) crystallises from alcohol in yellow prisms, m. p. 165° (Found: N, 11·8. $C_{10}H_{12}O_5N_2$ requires N, 11·7%).

4-*Nitro*-2 : 5-*dimethoxyaniline Hydrochloride*.—4-Nitro-2 : 5-dimethoxyacetanilide (10 g.) is boiled with 20% alcoholic hydrochloric acid (25 c.c.) for 1 hour. The grey crystals of the *hydrochloride* that separate on cooling (yield theoretical) crystallise from alcohol in yellow, metallic prisms, m. p. 160° (decomp.) (Found: N, 12·1. $C_8H_{11}O_4N_2Cl$ requires N, 11·9%).

4-*Nitro*-2 : 5-*dimethoxyaniline* forms yellow prisms, m. p. 153°.

Diazotisation of 4-*Nitro*-2 : 5-*dimethoxyaniline Hydrobromide*.—The solution obtained by diazotising 4-nitro-2 : 5-dimethoxyaniline hydrobromide (4 g.) in concentrated hydrobromic acid (20 c.c.) and water (25 c.c.) at 0° with 2·5 c.c. of 40% sodium nitrite is filtered, added cautiously to a solution of cuprous bromide in concentrated hydrobromic acid, and the mixture heated on a water-bath for a short time. The 2-bromo-5-nitroquinol dimethyl ether that separates is washed with concentrated hydrobromic acid and with water and crystallised from alcohol. The product, pale yellow prisms, m. p. 154°, does not depress the m. p. of 2-bromo-5-nitroquinol dimethyl ether obtained by bromination of nitroquinol dimethyl ether.

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THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, June 30th*, 1925.]

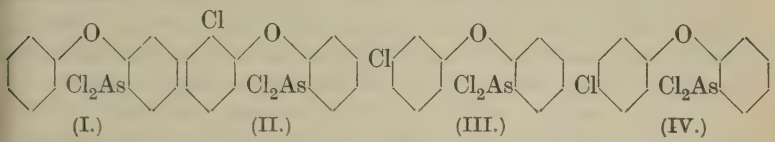
CCLXXI.—*The Relative Rates of Conversion of Phenoxyphenyldichloroarsine and its Chloro-derivatives into Chlorophenoxarsines.*

By ELWYN ROBERTS and EUSTACE EBENEZER TURNER.

IT was previously shown (Turner and Sheppard, this vol., p. 544) that *o*-phenoxyphenyldichloroarsine readily passes into 5-chlorophenoxarsine (there named 6-chlorophenoxarsine) when distilled under diminished pressure, and it was suggested that polarity effects might account for this then unusual ring-closure. It was therefore decided to test the effect, on the ring-closure, of a polar substituent in the dichloroarsine. In starting the work, the present authors were unaware of the fact that diphenylyl-*o*-arsenious chloride is readily converted into *oo'*-diphenylylenearsenious chloride (Aeschlimann, Lees, McCleland, and Nicklin, this vol., p. 66).

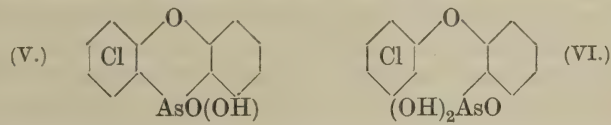
It having been found that *o*-phenoxyphenyldichloroarsine under-

went ring-closure at a readily measurable rate when heated at 200° in a current of carbon dioxide, it was decided to compare, under these conditions, the rate of ring-closure of the parent *o*-phenoxy-compound (I) and its *ortho*- (II), *meta*- (III), and *para*- (IV) chloro-derivatives :



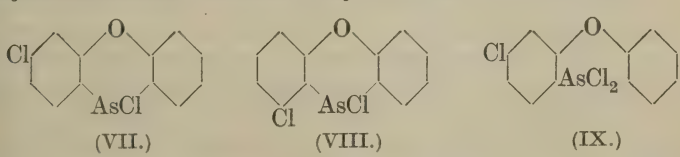
Compounds (II), (III) and (IV) were synthesised from the appropriate chlorophenol by processes similar to that originally used for the synthesis of (I). Preliminary experiments showed that whilst the compounds (II) and (IV) could be distilled under diminished pressure with only partial decomposition, compound (III) underwent very considerable ring-closure, a result which at first sight appeared to support the alternate polarities theory.

5 : 8- (see below) and 5 : 7-*Dichlorophenoxarsines* were prepared in two ways; first, by prolonged boiling of dichloroarsines (III) and (IV) under diminished pressure, and secondly by the reduction (hydrochloric–hydriodic–sulphurous acid method) of the corresponding chlorophenoxarsinic acids (V), the latter being obtained by the action of warm concentrated sulphuric acid on the corresponding chlorophenoxyphenylarsinic acids (VI) :



5 : 9-*Dichlorophenoxarsine* was prepared by boiling the corresponding phenoxydichloroarsine under diminished pressure.

The constitutions of three of the chlorophenoxarsines follow from their mode of formation from the corresponding dichloroarsines. That of the chlorophenoxarsine obtained from 2-m-*chlorophenoxyphenyldichloroarsine*, however, may be either (VII) or (VIII) :



5 : 8-Dichlorophenoxarsine (VII) has therefore been synthesised by a process which leaves no doubt as to its constitution. When 2 : 4-dichloronitrobenzene is warmed with 1 mol. of potassium phenoxide in phenol as solvent, the 2-chlorine atom is displaced by

phenoxyl. The resulting *5-chloro-2-nitrodiphenyl ether* is readily converted by the usual series of reactions into *4-chloro-2-phenoxyphenyldichloroarsine* (IX), and the latter, when heated at 200° in a current of carbon dioxide affords 5 : 8-dichlorophenoxarsine, identical in all respects with the product obtained from 2-*m*-chlorophenoxyphenyldichloroarsine. It also follows that the substance obtained by heating 2-m-*chlorophenoxyphenylarsinic acid* with concentrated sulphuric acid is 5 : 8-*dichlorophenoxarsinic acid*.

In order to compare their rates of ring-closure, the four dichloroarsines were heated simultaneously in the same bath kept at 200°. Through each dichloroarsine carbon dioxide was bubbled at the same rate, and the hydrogen chloride liberated was determined at intervals. In this way it was found (see p. 2012) that *o*-phenoxyphenyldichloroarsine (I) undergoes ring-closure much more readily than does its *m*-chloro-derivative (III), whilst the latter in turn undergoes ring-closure much more rapidly than the ortho- (II) or para- (IV) derivative, the last two compounds undergoing ring-closure at approximately equal rates.

This result appears to show conclusively that the polarising effect of the chlorine atom is not the sole determining influence affecting ring-closures of dichloroarsines to chlorophenoxarsines, just as the polarising effect of the oxygen atom can no longer be regarded as the main determining influence causing the ready formation of 5-chlorophenoxarsine itself.

The theory of alternate latent polarities requires compound (III) (combined effects of chlorine and oxygen) to pass more readily than (I) into a phenoxarsine, and (II) and (IV) to undergo ring-closure much less readily (opposed effects of chlorine and oxygen). A purely steric effect on the part of the chlorine atom would account for the observed fact that compound (I) undergoes ring-closure more readily than compound (III), but scarcely explains why (II) and (IV) pass into chlorophenoxarsines so much less readily. The main determining factor appears to be a steric one, modified by polar effects. In the case of compound (III), the steric outweighs the polar effect of the chlorine atom, whilst in the case of (II) and (IV) it enhances this effect. 4-Chloro-2-phenoxyphenyldichloroarsine (IX) (see below) is apparently even more readily converted into a phenoxarsine than *o*-phenoxyphenyldichloroarsine itself. This is in full agreement with a combined steric and polarity effect. In explaining the results obtained, Flürscheim's theory does not appear to present any advantages over the theory of alternate latent polarities, which, on this occasion at any rate, seems to be capable of definite interpretation, whilst the more subtle alternation of free affinity is not readily dealt with in the case of two key-atoms

having opposite effects. The observations of Altschul in connexion with the coupling of diazo-solutions with the isomeric nitrophenols are of interest in comparison with the present results (*Chem.-Ztg.*, 1898, **22**, 115).

When *o*-phenoxy- or 2-*o*-chlorophenoxy-phenylarsinic acid is heated with concentrated sulphuric acid, the corresponding phenoxarsinic acid is not obtained. Since each phenyl nucleus in diphenyl ether is readily monosulphonated, the different behaviour of the four phenoxyphenylarsinic acids may be explained as follows: Phenoxyphenylarsinic acid itself readily undergoes sulphonation in the unsubstituted phenyl nucleus, so that the final product is a sulphonic acid of the simple arsinic acid or of the phenoxarsinic acid. 2-*o*-Chlorophenoxyphenylarsinic acid, owing to combined polar and steric effects of the chlorine atom, undergoes sulphonation more rapidly than ring-closure. 2-*m*-Chlorophenoxyphenylarsinic acid shows a greater tendency to undergo ring-closure than to sulphonate, owing to the steric effect, on sulphonation, of the chlorine atom, whilst 2-*p*-chlorophenoxyphenylarsinic acid is readily converted into a phenoxarsinic acid, owing to the presence of a chlorine atom in the position at which sulphonation would occur.

The mechanism of the hydrochloric–hydriodic–sulphurous acid reduction of arsinic acids to dichloroarsines is imperfectly understood. In the reduction of 4-chloro-2-phenoxyphenylarsinic acid, free iodine is liberated as reduction proceeds, and appears as a surface film, which, although readily broken up by agitation, continually reappears, whilst any arsinic acid remains unreduced. Suddenly the oily dichloroarsine–oxychloride–acid mixture solidifies, owing to its conversion into dichloroarsine, and at once the iodine film disappears. Similar, although less definite, changes occur in other cases, and it would therefore appear clear that hydriodic acid is the essential reducing agent, being immediately oxidised in presence of even small quantities of an arsinic acid.

Experimental.

Preparation of 2-, 3-, *and* 4-*Chloro*-2′-*nitrodiphenyl Ethers.*—The method adopted for the preparation of these compounds has been that previously employed, using *o*-chloronitrobenzene (1 mol.), a phenol (2 mols.), potassium hydroxide (1 mol.), and water (0·3 mol.) in presence of copper bronze. The yields given below are calculated on the chloronitrobenzene. If the proportion of alkali be increased (say, to 1·5 mols.), unworkable tars result, but in the case of the condensation with *m*-chlorophenol, a substance only obtainable with difficulty, the proportion of phenol may be reduced to 1 mol. without seriously decreasing the yield.

2-*Chloro*-2′-*nitrodiphenyl ether* was obtained in 55% yield, forms yellow, hexagonal prisms or plates from alcohol, and has m.p. 48°, b. p. 209°/9 mm. (Found: NO_2, 18·8. $C_{12}H_8O_3NCl$ requires NO_2, 18·4%).

3-*Chloro*-2′-*nitrodiphenyl ether*, obtained in 58% yield, is a yellow oil, b. p. 204°/8 mm. [Found (crude substance) NO_2, 17·3%]. The *m*-chlorophenol required was obtained by Hodgson's method (*Brit. Pat.* 200714) from *m*-chloroaniline. The addition of copper sulphate to the diazo-solution appears to improve the yield (94%) slightly. The *m*-chloroaniline used was readily prepared in almost theoretical yield by reducing *m*-chloronitrobenzene by the iron–ferric chloride method (below).

4-*Chloro*-2′-*nitrodiphenyl ether*, obtained in 75% yield, separates from alcohol in yellow needles, m. p. 44—45°, b. p. 208°/11 mm., or 220°/20 mm. (Found: Cl, 14·7; NO_2, 18·9. $C_{12}H_8O_3NCl$ requires Cl, 14·2; NO_2, 18·4%).

Preparation of Aminodiphenyl Ethers.—The method previously adopted for the reduction of nitrodiphenyl ethers has been abandoned in favour of the following, which gives excellent yields. A mixture of nitro-compound (1 part), iron filings (1·5 parts), and water (1 part) was heated for about 10 minutes in boiling water, with thorough shaking. A gram of ferric chloride for each 100 g. of iron was then added and the whole shaken and heated until a reaction set in. The reaction was controlled if necessary by removal from the bath, and finally completed by heating in boiling water for an hour. The cooled product was shaken with ether, filtered, and the iron residue washed with ether. The ethereal solution was shaken with an excess of hydrochloric acid, when the base separated as the hydrochloride. The iron residues become warm on exposure to air, owing to rapid oxidation.

All the amino-compounds are stable, and distil unchanged in a vacuum.

o-*Aminodiphenyl ether*, obtained in almost theoretical yield, forms an *acetyl* derivative, colourless prisms from light petroleum (b. p. 80—100°) (Found: N, 6·4. $C_{14}H_{13}O_2N$ requires N, 6·2%).

2-*Chloro*-2′-*aminodiphenyl ether*, obtained in 90% yield, separates from light petroleum (b. p. 80—100°) in white prisms, m. p. 44—45°, b. p. 185°/9 mm. The *hydrochloride* forms colourless, irregular plates, m. p. 171—173° (Found: HCl, 14·6. $C_{12}H_{10}ONCl,HCl$ requires HCl, 14·3%).

3-*Chloro*-2′-*aminodiphenyl ether* was obtained in 91% yield, and is a colourless oil, b. p. 195°/13 mm. The *hydrochloride*, colourless aggregates of prisms, has m. p. 149—151° (Found: HCl, 14·4%).

The *benzoyl* derivative separates from dilute alcohol in clusters of needles, m. p. 106°.

4-*Chloro*-2′-*aminodiphenyl ether*, obtained in 94% yield by the iron method, and in 84% yield by the alcoholic stannous chloride method, is a yellow oil, b. p. 202°/15 mm. The *hydrochloride* forms colourless prisms, m. p. 190—191° (Found : HCl, 14·3%), and the *benzoyl* derivative, hair-like needles from dilute alcohol, m. p. 108—109°.

Preparation of Phenoxyphenylarsinic Acids.—These acids were prepared by the following modification of the usual method :

The diazo-solution obtained from amine hydrochloride (1 mol.), and hydrochloric acid (1·5 mols.), etc., was neutralised with sodium hydrogen carbonate (0·5 mol.), and treated with a little copper sulphate solution. This solution was then slowly added to an arsenite solution (at 50—60°), containing arsenious oxide (0·75 mol.), sodium hydroxide (2 mols.), sodium carbonate (0·7 mol.), water (7 mols.), and a little copper sulphate. It was found advantageous not to use benzene to prevent frothing, because the by-products were obtained as brown solids which could readily be removed by filtration, the filtrate affording pure arsinic acids after acidification. The acids were dried at 100° before analysis.

o-*Phenoxyphenylarsinic acid* was obtained in 32% yield and separates from alcohol in needles, m. p. 167—168°.

2-o-*Chlorophenoxyphenylarsinic acid*, obtained in 18% yield, crystallises from alcohol or water in needles, m. p. 195—195·5° (Found : As, 22·8. $C_{12}H_{10}O_4ClAs$ requires As, 22·8%).

2-m-*Chlorophenoxyphenylarsinic acid* (yield, 18%) separates from dilute alcohol in rounded, hexagonal plates, m. p. 177—179° (Found : As, 23·0%).

2-p-*Chlorophenoxyphenylarsinic acid* was obtained in 24% yield, and forms cubes (from alcohol), m. p. 187—188° (Found : As, 22·8%).

Preparation of Chlorophenoxyphenyldichloroarsines.—The arsinic acids were reduced in warm concentrated hydrochloric acid suspension with sulphur dioxide in presence of a little potassium iodide. The crude dichloroarsines were converted into the corresponding oxides by dissolving in alcoholic sodium hydroxide containing sodium sulphite, and pouring the product into dilute sulphuric acid. In this way, all traces of iodine were removed, and the oxides, when warmed with concentrated hydrochloric acid, afforded pure dichloroarsines. The yields were almost theoretical.

2-o-*Chlorophenoxyphenyldichloroarsine* is a pale yellow oil, boiling with only partial decomposition at about 217°/8 mm. [Found : Cl (attached to arsenic), 20·7. $C_{12}H_8OCl_3As$ requires Cl, 20·3%].

2-m-*Chlorophenoxyphenyldichloroarsine*, is a pale yellow oil boiling with advanced decomposition at about 220°/10 mm. [Found, Cl (attached to arsenic), 20·8%].

2-p-*Chlorophenoxyphenyldichloroarsine*, pale yellow, prismatic needles from petroleum (b. p. 80—100°), has m. p. 67—68°, and boils with only partial decomposition at about 220°/10 mm. [Found: Cl (attached to arsenic), 20·3%].

The analysis of the dichloroarsines and of the chlorophenoxarsines has been effected by a simplified method: The chloroarsine was dissolved in alcohol, a slight excess of sodium hydrogen carbonate added, the solution warmed, just acidified with dilute sulphuric acid, neutralised with precipitated calcium carbonate, and titrated against *N*/10-silver nitrate.

Preparation of Chlorophenoxarsinic Acids.—8-*Chlorophenoxarsinic acid.* Two grams of 2-*m*-chlorophenoxyphenylarsinic acid were heated with 15 c.c. of concentrated sulphuric acid at 100° for 15 minutes, the solution then poured into water, and the precipitate collected. It was found impossible to obtain a pure compound by recrystallisation, and purification was ultimately effected by adding excess of sodium hydroxide to a solution of the *sodium* salt (colourless leaflets), when the latter was precipitated in the pure state, and gave rise to an acid which crystallised from alcohol in prisms, m. p. 250—252° (Found: As, 24·3. $C_{12}H_8O_3ClAs$ requires As, 24·2%).

7-*Chlorophenoxarsinic acid.* This acid separated on diluting the concentrated sulphuric acid solution; it crystallised from alcohol in colourless plates or prisms, m. p. 240—242° (Found: As, 23·7%).

When *o*-phenoxyphenylarsinic acid or its *o*-chloro-derivative was heated with concentrated sulphuric acid and the product diluted, no separation of solid occurred, and neutralisation by barium carbonate, finally followed by treatment of the barium salt with sulphuric acid, gave deliquescent sulphonic acids, which were not further investigated.

Preparation of Dichlorophenoxarsines.—(a) *From chlorophenoxarsinic acids.* 8-Chlorophenoxarsinic acid, when reduced by the usual method in the warm, gave 5 : 8-*dichlorophenoxarsine*, which separates from petroleum (b. p. 80—100°) in colourless intersecting circular plates, m. p. 125° [Found: Cl (attached to arsenic), 11·5. $C_{12}H_7OCl_2As$ requires Cl, 11·3%].

7-Chlorophenoxarsinic acid, when similarly reduced, gave a mixture which was separated by repeated crystallisation from petroleum–chloroform solution. 5 : 7-*Dichlorophenoxarsine* was obtained as almost colourless rhombs, m. p. 144—145° [Found: Cl (attached to arsenic), 11·3%], together with an arsenic-free *substance* forming yellow laminæ, m. p. 119—120°.

(b) *From chlorophenoxyphenyldichloroarsines.* The dichloroarsines were either allowed to boil gently under reflux under diminished pressure for 6 hours, or heated for a similar period at 200° in a current of carbon dioxide, and the residual crude chlorophenoxarsine was crystallised from chloroform–petroleum mixtures.

5 : 9 - *Dichlorophenoxarsine,* from 2 - *o* - chlorophenoxyphenyldichloroarsine, forms pale yellow needles, m. p. 99° [Found : Cl (attached to arsenic), 11·3%].

Synthesis of 5 : 8 - *Dichlorophenoxarsine.* — 2 : 4-*Dichloronitrobenzene.* As details of the preparation of this substance are not to be found in the literature, they are given here : *m*-Dichlorobenzene (1 mol.) was dissolved in nitric acid (*d* 1·5; 4·5 mols.) with efficient cooling, and the solution then warmed for 10 minutes at 70°. On pouring into ice and water, the nitro-compound separated as a solid, which after being melted under hot water melted at 33° (Beilstein and Kurbatov, *Annalen*, 1876, **182**, 97, give the same figure).

5-*Chloro*-2-*nitrodiphenyl ether.* 2 : 4-Dichloronitrobenzene (1 mol.) was added to a warm solution containing potassium hydroxide (1 mol.), phenol (2 mols.), and water (0·3 mol.). A vigorous reaction at once set in, without addition of copper bronze, and was completed by heating at 100° for 10 minutes. The product, after being worked up as usual, afforded the theoretical yield of the chloronitrodiphenyl ether, which crystallises from alcohol or petroleum (b. p. 80—100°) in prisms, m. p. 85° (Found : Cl, 14·3; NO_2, 17·8. $C_{12}H_8O_3NCl$ requires Cl, 14·2; NO_2, 18·4%). Using half the above proportion of phenol, the same result was obtained.

5-*Chloro*-2-*aminodiphenyl ether.* The last-named nitro-compound was reduced by the iron–ferric chloride method, when the amine hydrochloride was obtained in 95% yield as needles of indefinite m. p. (Found : HCl, 14·2. $C_{12}H_{10}ONCl,HCl$ requires HCl, 14·3%).

4-*Chloro*-2-*phenoxyphenylarsinic acid.* This acid, obtained in 25% yield from the amine hydrochloride in the usual manner, forms colourless, hairy tufts of needles from dilute alcohol, and has m. p. 182° (Found : As, 22·3. $C_{12}H_{10}O_4ClAs$ requires As, 22·8%).

4-*Chloro*-2-*phenoxyphenyldichloroarsine* (see introduction), pale yellow, regular cubes or octahedra from petroleum (b. p. 80—100°), has m. p. 91—92°, and possesses an objectionable odour [Found : Cl (attached to arsenic), 20·1. $C_{12}H_8OCl_3As$ requires Cl, 20·3%].

5 : 8-*Dichlorophenoxarsine.* A weighed quantity of 4-chloro-2-phenoxyphenyldichloroarsine was heated at 200° in a current of pure carbon dioxide. Hydrogen chloride was evolved rapidly, the percentage conversion into dichlorophenoxarsine at the end of 2, 3, and 8 hours being about 45, 55, and 65, respectively. Heating was then discontinued. The product became solid on cooling, and

was once crystallised from light petroleum (b. p. 80—100°). It then melted at 125°, possessed the highly characteristic crystalline form of the dichloroarsine obtained from 2-*m*-chlorophenoxyphenyldichloroarsine, and did not depress the m. p. of this phenoxarsine [Found : Cl (attached to arsenic), 11·7%].

Rates of Conversion of Phenoxyphenyldichloroarsines into Chlorophenoxarsines.—About 1 g. of each of the four dichloroarsines (I—IV) was placed in a test-tube fitted as a wash-bottle, with a capillary carbon dioxide ingress tube passing to the bottom of the test-tube. The egress tube was connected to an absorption flask containing *N*/10-potassium hydroxide solution in each case. All four tubes were simultaneously plunged into a stirred oil-bath kept at 200° ± 1°, and an equal current of pure carbon dioxide allowed to bubble through each. At intervals of 1 hour, the absorption flasks were replaced by similar ones, this operation being carried out in a uniform routine manner, so that the exact time interval obtained for each substance. The results are expressed below in terms of percentage decomposition.

	Percentage decomposition.			
Time (hours).	I.	II.	III.	IV.
1	23·7	1·86	8·90	1·09
2	38·2	6·08	23·4	4·65
3	45·7	11·2	29·3	11·3
4	49·5	15·5	33·0	17·0
5	53·5	19·7	35·5	20·5
6	56·6	24·3	37·8	27·0

The expenses of this investigation were partly defrayed by a grant obtained from the Chemical Society, for which the authors desire to express their thanks.

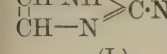
East London College,
University of London. [*Received, June 12th,* 1925.]

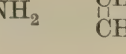
CCLXXII.—2-*Amino*-4 : 5-*dimethylglyoxaline.*

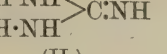
By [the late] Richard Burtles and Frank Lee Pyman.

4(5)-Amino-5(4)-methylglyoxaline (Fargher, J., 1920, **117**, 668), 4-amino-1 : 5-dimethylglyoxaline, and 5-amino-1 : 4-dimethylglyoxaline (Pyman, J., 1922, **121**, 2616) behave like typical aromatic amines in yielding benzylidene derivatives, and diazo-solutions which couple with sodium β-naphthoxide. The so-called 2-aminoglyoxaline (I), however, neither yields a benzylidene derivative (Fargher and Pyman, J., 1919, **115**, 217) nor does it behave normally with sodium nitrite (Pyman and Timmis, *J. Soc. Dyers Col.*, 1922, **38**,

269). It seems, therefore, to react rather according to the alternative tautomeric formula, that of 2-imino-3 : 4-dihydroglyoxaline

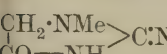

(I.)

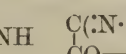

(II.)

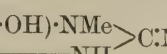

(III.)

(II), put forward by Fargher and Pyman, and it may be noted that some other amino-compounds capable of similar tautomerism, for example, 2-aminopyridine, fail to react smoothly with nitrous acid.

On the other hand, the 8-aminopurines, for example, 8-aminoxanthine (III), which contain an amino-group in the 2-position of the glyoxaline nucleus, yield diazo-compounds which couple with R-salt (H. Fischer, *Z. physiol. Chem.*, 1909, **60**, 69). The 8-aminopurines differ from 2-aminoglyoxaline in that there is no possibility of substitution in their case at the 4- and 5-positions of the glyoxaline ring, and it seemed possible that this difference in structure might be the cause of the difference in behaviour. Some support appeared to be lent to this view by the fact that creatinine (IV) gives with nitric acid and sodium nitrite a mixture of oximinocreatinine (V) with oximinomethylhydantoin (Schmidt and Thumann, *Arch. Pharm.*, 1912, **250**, 352), and it was thought that the action of nitrous acid on 2-aminoglyoxaline might lead to the formation of an oximino-derivative (VI). To test this point, we have prepared

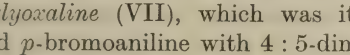

(IV.)


(V.)


(VI.)

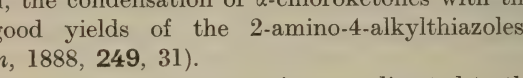
2-*amino*-4 : 5-*dimethylglyoxaline* (VIII), which cannot yield an oximino-compound of this type, and find that in general its behaviour towards nitrous acid in the presence of acid or alkali resembles that of 2-aminoglyoxaline. Consequently, the failure of 2-aminoglyoxaline to behave normally with nitrous acid cannot be attributed to the suggested cause.

The 2-amino-4 : 5-dimethylglyoxaline (VIII) required for this purpose was prepared by the reduction of 2-p-*bromobenzeneazo*-4 : 5-*dimethylglyoxaline* (VII), which was itself obtained by coupling diazotised *p*-bromoaniline with 4 : 5-dimethylglyoxaline. Since the


(VII.) (VIII.)

synthesis of 4 : 5-dimethylglyoxaline is long and tedious, an alternative method of preparing the amine was sought in the condensation

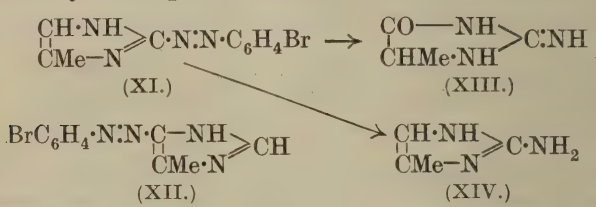
of α-bromoethyl methyl ketone (IX) with guanidine (X), but the required substance could not even be identified with certainty



(IX.) (X.)

amongst the products of the reaction, although an analogous reaction, the condensation of α-chloroketones with thiocarbamides, gives good yields of the 2-amino-4-alkylthiazoles (Traumann, *Annalen*, 1888, **249**, 31).

In these circumstances, attention was directed to the preparation of 2-*amino*-4(5)-*methylglyoxaline* (XIV), which, it was expected, could be made in quantity from the readily accessible 4(5)-methylglyoxaline. On treating this base with diazotised *p*-bromoaniline, the expected mixture of 2- and 5(4)-p-*bromobenzeneazo*-4(5)-*methylglyoxalines* (XI and XII) with the bis-azo-compound was obtained. The constitution of the 2-isomeride [and therefore of the 5(4)-isomeride also] was readily established through its reduction to alacreatinine (XIII) by means of zinc dust and acetic acid, but, unfortunately, attempts to reduce it smoothly to 2-amino-4(5)-methylglyoxaline, by means of stannous chloride, failed. Here again alacreatinine was obtained together with a substance which was probably the required amine.



(XI.) (XIII.)

(XII.) (XIV.)

Experimental.

2-p-*Bromobenzeneazo*-4 : 5-*dimethylglyoxaline* (VII).—4 : 5-Dimethylglyoxaline hydrochloride (4·12 g.) was added to an aqueous solution of hydrated sodium carbonate (59 g.) in water (300 c.c.), and to the turbid liquor, the product of diazotising *p*-bromoaniline (5·37 g.) in concentrated hydrochloric acid (32 c.c.) and water (100 c.c.) with sodium nitrite (3 g.) was added. After keeping over-night, the insoluble product was collected and crystallised from alcohol (7·15 g.; yield = 82%).

2-p-*Bromobenzeneazo*-4 : 5-*dimethylglyoxaline* crystallises from alcohol in light brown needles, m. p. 213—214° (corr.) (Found : N, 19·9; Br, 29·1. $C_{11}H_{11}N_4Br$ requires N, 20·1; Br, 28·7%). It seems to cause irritation of the skin and swelling of the eyelids.

On treatment with cold hydrochloric acid, it yields a sparingly soluble *hydrochloride* (orange-yellow needles, decomp. 135°), which resinifies when heated with dilute hydrochloric acid (Found : Cl, 11·6. $C_{11}H_{11}N_4Br,HCl$ requires Cl, 11·3%).

Reduction.—The above azo-compound (2·79 g.) was reduced by heating at 100° with stannous chloride (5·6 g. hydrated) in concentrated hydrochloric acid (13 c.c.) and water (50 c.c.) until almost completely decolorised. After removing tin by hydrogen sulphide, the solution was concentrated to low bulk, and made alkaline; *p*-bromoaniline was then partly precipitated and partly removed by ether. The mother-liquor was acidified with hydrochloric acid, evaporated to dryness, and extracted with alcohol; the extract gave on evaporation 2-amino-4 : 5-dimethylglyoxaline hydrochloride (1·02 g.; yield = 69%).

2-*Amino*-4 : 5-*dimethylglyoxaline hydrochloride* (VIII) crystallises from alcohol in fine, colourless needles, m. p. 289° (corr.) (Found : C, 40·4; H, 7·0; N, 28·1; Cl, 24·4. $C_5H_9N_3,HCl$ requires C, 40·7; H, 6·8; N, 28·5; Cl, 24·0%). It is very easily soluble in water or alcohol, and is best purified through the carbonate, which is precipitated on mixing this salt with sodium carbonate in strong aqueous solution, and may be recrystallised quickly from water. The *carbonate*, m. p. 144° (corr.), contains 1 H_2O, and is readily soluble in hot water, but much less soluble in cold water. It is insoluble or very sparingly soluble in most organic solvents. Its aqueous solution is alkaline and gradually darkens on heating, yielding resinous products [Found in air-dried substance : C, 43·4, 43·5; H, 7·2, 7·3; N, 28·1. $(C_5H_9N_3)_2,H_2CO_3,H_2O$ requires C, 43·7; H, 7·3; N, 27·8%]. The *picrate* crystallises from water in yellow needles, m. p. 245° (corr.) (Found : N, 24·5. $C_5H_9N_3,C_6H_3O_7N_3$ requires N, 24·7%).

Reactions with Nitrous Acid.—Both 2-amino-4 : 5-dimethylglyoxaline and 2-aminoglyoxaline react sluggishly with nitrous acid in the presence of dilute or concentrated hydrochloric acid or of 25% acetic acid, giving solutions from which neither the original material nor any useful quantity of other crystalline substances could be isolated, but which give deep colours on treatment with sodium hydroxide. A difference in behaviour, however, was observed where 23% nitric acid was employed, for here, after treatment with sodium nitrite and keeping for 2 days, the solution from 2-aminoglyoxaline deposited a red solid, the filtrate from which gave a purple solution with sodium hydroxide, whilst the solution from 2-amino-4 : 5-dimethylglyoxaline remained clear and gave a pale yellow solution with either sodium hydroxide or sodium β-naphthoxide. Both amines give deeply coloured solutions with

either sodium nitroprusside and aqueous sodium hydroxide, or with amyl nitrite and sodium ethoxide in alcoholic solution. Since solutions of both amines in aqueous sodium hydroxide gradually darken on keeping, it is possible that the main effect of nitrous acid upon them is one of oxidation, for both bases are readily oxidised; thus 2-amino-4 : 5-dimethylglyoxaline immediately reduces cold aqueous acid permanganate or ammoniacal silver nitrate.

2-*Acetylamino*-4 : 5-*dimethylglyoxaline*, prepared by boiling the above carbonate with acetic anhydride and fused sodium acetate for 1 hour, crystallised from water in colourless needles, m. p. 270° (corr.) (Found : N, 27·6. $C_7H_{11}ON_3$ requires N, 27·5%). It is soluble in dilute hydrochloric acid and in aqueous sodium hydroxide, but insoluble in aqueous sodium carbonate. After treatment with hydrochloric acid and sodium nitrite, it gives no coloration with sodium β-naphthoxide. It instantly decolorises cold aqueous potassium permanganate.

2-Amino-4 : 5-dimethylglyoxaline does not yield a benzylidene derivative.

p-*Bromobenzeneazo-derivatives of* 4(5)-*Methylglyoxaline*.—The diazo-solution from *p*-bromoaniline (34·4 g.), hydrochloric acid (260 c.c. conc.), water (600 c.c.), and sodium nitrite (14 g.) was added to a stirred ice-cold solution of 4(5)-methylglyoxaline (16·4 g.) and hydrated sodium carbonate (350 g.) in water (1·6 l.). After keeping over-night, the insoluble azo-compounds were collected, and the filtrate was treated with diazotised *p*-bromoaniline (2 g.) [to utilise the 4(5)-methylglyoxaline remaining in excess on account of the formation of the bis-azo-compound], when a further separation of azo-compounds occurred. The total material was extracted several times with cold 2·5% hydrochloric acid (240 c.c. each time), when the very dark-red bis-azo-compound (10 g., crude, m. p. 100—102°) remained undissolved. The filtrate was basified with sodium carbonate, and the product crystallised from alcohol, when nearly pure 2-*p*-bromobenzeneazo-4(5)-methylglyoxaline, *ca.* 20 g., m. p. 219°, separated, followed by crops of lower m. p. (204—210°). The latter were mixed with cold dilute hydrochloric acid, when the sparingly soluble 5(4)-*p*-bromobenzeneazo-4(5)-methylglyoxaline hydrochloride separated, and the filtrate from this, when basified, gave more of the crude 2-azo-compound. After repetition of these operations, there were obtained 25 g. of the 2-azo-compound (47%) and 7·5 g. of the hydrochloride of the 5(4)-azo-compound (12%).

2-p-*Bromobenzeneazo*-4(5)-*methylglyoxaline* (XI) crystallises from alcohol in fine yellow needles, m. p. 225—226° (corr.) (Found : C, 45·2; H, 3·6; N, 21·1. $C_{10}H_9N_4Br$ requires C, 45·3; H, 3·4

N, 21·1%). Its hydrochloride is very easily soluble in dilute hydrochloric acid.

5(4)-p-*Bromobenzeneazo*-4(5)-*methylglyoxaline* (XII) crystallises from alcohol in irregular, brown prisms, m. p. 238° (corr.) (Found : C, 45·1 ; H, 3·6. $C_{10}H_9N_4Br$ requires C, 45·3 ; H, 3·4%). The *hydrochloride* is sparingly soluble in dilute hydrochloric acid, from which it crystallises in fine yellow needles or long, yellow-red prisms, m. p. 188° (decomp. ; corr.).

Reduction of 2-p-*Bromobenzeneazo*-4(5)-*methylglyoxaline*.—A. *With zinc dust and acetic acid.* Zinc dust (9 g.) was added gradually to a solution of the azo-compound (5·3 g.) in a boiling mixture of glacial acetic acid (20 c.c.) with water (40 c.c.). Zinc was removed by hydrogen sulphide, and the solution was mixed with hydrochloric acid and evaporated to dryness. After basifying with aqueous sodium carbonate, *p*-bromoaniline (2·3 g.) was collected by means of ether, and the aqueous solution was acidified with hydrochloric acid, evaporated to dryness, and extracted with alcohol, which left sodium chloride and some ammonium chloride undissolved. The alcoholic extract was mixed with alcoholic picric acid and gave 1·8 g. (yield 26%) of pure alacreatinine picrate, m. p. 212° (decomp. ; corr. : after sintering earlier) (Found : C, 35·3 ; H, 3·2. Calc. : C, 35·1 ; H, 2·9%). This identification was confirmed by the preparation of the hydrochloride, which had m. p. 202° (corr.) (compare Fargher and Pyman, *loc. cit.*).

B. *With hot stannous chloride.* Stannous chloride (33·6 g., hydrated) in concentrated hydrochloric acid (66 c.c.) was added to a hot solution of the azo-compound (15·9 g.) in hydrochloric acid (12 c.c.) and water (300 c.c.). Decoloration took place at once, and, proceeding as in A, *p*-bromoaniline (6·5 g.), and a mixture of picrates (from water instead of alcohol), amounting to 10·7 g., m. p. 155—180°, were collected. After a tedious process of crystallisation from water and alcohol, the latter gave a sparingly soluble picrate (0·4 g., m. p. >300° ; probably guanidine picrate), alacreatinine picrate (2·3 g. ; m. p. 210—211° ; yield 11%), and 2-*amino*-4(5)-*methylglyoxaline picrate* (XIV) (2·05 g., yield 10%). This salt crystallised from alcohol in brownish-yellow nodules, m. p. 186—187° (corr.) (Found : C, 37·2 ; H, 3·6. $C_4H_7N_3,C_6H_3O_7N_3$ requires C, 36·8 ; H, 3·1%). The hydrochloride, prepared from the picrate in the usual way, was not obtained crystalline, but its aqueous solution resembled that of 2-aminoglyoxaline hydrochloride in its behaviour towards nitrous acid in acid and alkaline solution.

C. *With cold stannous chloride.* Stannous chloride (12·0 g., hydrated) in concentrated hydrochloric acid (30 c.c.) was added to a solution of the azo-compound (6·6 g.) in 3% hydrochloric acid

(66 c.c.) at 0°. After keeping over-night at the laboratory temperature, the solution had become clear and colourless, and was worked up as before, when *p*-bromoaniline (3·5 g.) was obtained together with a mixture of picrates from which 3·2 g. (yield 38%) of pure alacreatinine picrate were isolated.

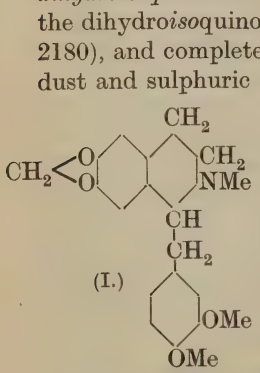
One of us (R. B.) is indebted to the Department of Scientific and Industrial Research for a grant which he desires gratefully to acknowledge.

MUNICIPAL COLLEGE OF TECHNOLOGY,
UNIVERSITY OF MANCHESTER. [*Received, July 8th,* 1925.]

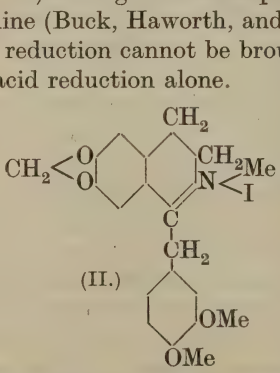
CCLXXIII.—*A Synthesis of* dl-*Dicentrine.*

By ROBERT DOWNS HAWORTH, WILLIAM HENRY PERKIN, jun., and JOHN RANKIN.

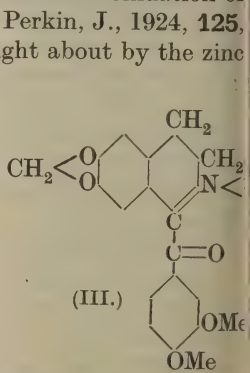
THE observation that 1-veratrylnorhydrohydrastinine is converted into 6′-nitroveratrylnorhydrohydrastinine by the action of nitric acid (Haworth and Perkin, this vol., p. 1450) has led to an examination of the action of nitric acid on 1-*veratrylhydrohydrastinine* (I). This base was obtained by converting homoveratroylhomopiperonylamine into 1-veratryl-6 : 7-methylenedioxydihydro*iso*quinoline (Haworth, Perkin, and Rankin, J., 1924, **125**, 1694), the *methiodide* (II) of which was made into the more soluble methochloride, and reduced to 1-veratrylhydrohydrastinine (I), first by zinc dust and sulphuric acid and then electrolytically. This procedure is advisable when the crude methiodide is employed, because this contains the *methiodide* of 6 : 7-*methylenedioxy*-3′ : 4′-*dimethoxy*-1-*benzoyl*-3 : 4-*dihydro*isoquinoline (III) arising from the spontaneous oxidation of the dihydro*iso*quinoline (Buck, Haworth, and Perkin, J., 1924, **125**, 2180), and complete reduction cannot be brought about by the zinc dust and sulphuric acid reduction alone.



(I.)



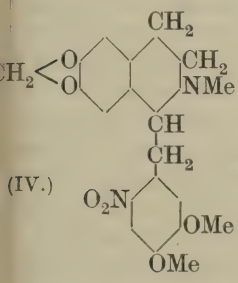
(II.)

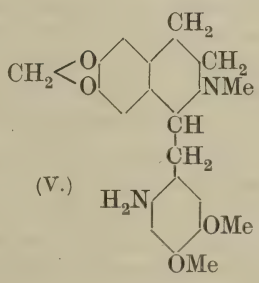


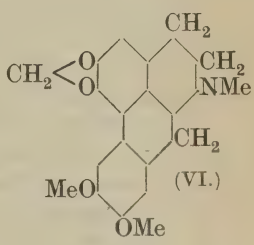
(III.)

1-Veratrylhydrohydrastinine (I) is a syrup from which a crystalline *hydrochloride, hydriodide* and *picrate* have been obtained. When

the base (I) was nitrated in acetic acid solution, 6′-*nitroveratrylhydrohydrastinine* (IV) was obtained as a buff-coloured, crystalline mass, from which a crystalline *hydriodide* and *picrate* have been prepared. The nitro-base (IV) was readily reduced to 6′-*aminoveratrylhydrohydrastinine* (V) by stannous chloride and hydrochloric acid, and although this substance has not been obtained in the crystalline state, a well-defined *dihydrochloride* has been prepared. The solution of the dihydrochloride yields an intense blue coloration on the addition of ferric chloride, indicating that the positions occupied by the nitro- and amino-groups are those represented in (IV) and (V) respectively.


(IV.)


(V.)


(VI.)

6′-Aminoveratrylhydrohydrastinine (V) was diazotised and treated with copper powder under conditions similar to those which Gadamer employed for the conversion of aminolaudanosine into *dl*-glaucine (*Arch. Pharm.*, 1911, **249**, 680), and a crystalline base, $C_{20}H_{21}O_4N$, m. p. 178—179°, was isolated in a yield of about 15%. The method of synthesis outlined above seems to us to leave no doubt that the synthetical alkaloid is dl-*dicentrine*, and on resolution this should yield an optically active base, identical with naturally occurring dicentrine. We are now engaged in an attempt to prepare considerable quantities of the *dl*-base for the purposes of this resolution and to improve the yields in the various stages of the synthesis; a more complete description of the preparation and properties of these substances is reserved for a future communication. The *dl*-base (VI) yields crystalline salts, the *methiodide* being particularly characteristic, whilst the *hydrochloride* and *picrate* also have been obtained. It should be mentioned that the synthetic base exhibits all those colour reactions with concentrated sulphuric acid, Erdmann's, Fröhde's and Mandelin's reagents which are characteristic of naturally occurring dicentrine (Asahina, *Arch. Pharm.*, 1909, **247**, 202).

Experimental.

1-*Veratryl*-6 : 7-*methylenedioxydihydroisoquinoline Methiodide* (II).—Homoveratroylhomopiperonylamine (20 g.) was converted into 1-veratryl-6 : 7-methylenedioxydihydro*iso*quinoline as described by Haworth, Perkin, and Rankin (*loc. cit.*), the total basic material extracted with benzene, dried over potassium carbonate, concentrated, and boiled with methyl iodide (12 c.c.), when a reddish-brown oil separated which gradually hardened; after 4 hours, the mass of yellow crystals (25 g.) was collected. This crude material, m. p. 228°, was usually employed for reduction purposes.

The *methiodide* is sparingly soluble in water and alcohol, and crystallises from boiling alcohol in beautiful, lustrous, straw-yellow plates, m. p. 239—240° (Found : C, 51·6; H, 4·9. $C_{20}H_{22}O_4NI$ requires C, 51·4; H, 4·7%).

6 : 7-*Methylenedioxy*-3′ : 4′-*dimethoxy*-1-*benzoyl*-3 : 4-*dihydro*iso*quinoline Methiodide* (III).—As this substance probably occurs in the crude methiodide described above, a small quantity was prepared for comparison with the above methiodide by boiling a benzene solution of 6 : 7-methylenedioxy-3 : 4-dimethoxy-1-benzoyl-3 : 4-dihydro*iso*quinoline (Buck, Haworth, and Perkin, *loc. cit.*) with excess of methyl iodide for several hours, when crystals separated which recrystallised from alcohol in amber-coloured rhombs, m. p. 232—233° (decomp.), sparingly soluble in water and alcohol (Found : C, 50·0; H, 4·2. $C_{26}H_{20}O_5NI$ requires C, 49·9; H, 4·2%).

1-*Veratrylhydrohydrastinine* (I).—The crude methiodide (25 g.) obtained as described above was suspended in water (500 c.c.) and digested with freshly-precipitated silver chloride for 4 hours, filtered off, and reduced with excess of zinc dust and dilute sulphuric acid for ½ hour. After filtration, the pale yellow solution was concentrated to 200 c.c., acidified with dilute sulphuric acid (50 c.c.), and reduced in an electrolytic cell with 5 amperes for 12 hours, when the solution became colourless and a mass of crystals separated. These were dissolved by warming, filtered, the base liberated by the addition of ammonia, extracted with chloroform, dried with potassium carbonate and evaporated, when an oil (12 g.) remained which could not be induced to crystallise. The *hydrochloride* was prepared by dissolving the base in dilute hydrochloric acid, and concentrating, when the salt separated in colourless, rhombic plates, m. p. 215—216°, which are readily soluble in alcohol and water (Found : C, 63·5; H, 6·4. $C_{20}H_{24}O_4NCl$ requires C, 63·6; H, 6·4%). The *hydriodide* was precipitated, by addition of potassium iodide to a hot solution of the hydrochloride, as an oil, which slowly hardened; it crystallised from water containing a little methyl alcohol in colour-

less, elongated prisms, m. p. 180—182° (Found : C, 51·2; H, 5·2. $C_{20}H_{24}O_4NI$ requires C, 51·2; H, 5·1%). It is soluble in methyl or ethyl alcohol, but sparingly so in water. The *picrate* was prepared in alcoholic solution, in which it was sparingly soluble, and crystallised from alcohol–glacial acetic acid in orange-yellow prisms, m. p. 188—189° (decomp.).

6′-*Nitroveratrylhydrohydrastinine* (IV).—Veratrylhydrohydrastinine (5 g.) dissolved in glacial acetic acid (25 c.c.) was treated at 5—10° with concentrated nitric acid (10 c.c.) which had been previously warmed with carbamide. After ¼ hour the dark brown nitration mixture was poured into water, when a brown slime separated. The mixture was digested for ½ hour with excess of ammonia, the liquid decanted from the semi-solid mass, and the latter boiled with dilute hydrochloric acid and animal charcoal, filtered, made alkaline with ammonia, and the crude buff-coloured nitro-base (4 g.) collected. This material is sufficiently pure for reduction purposes, but in order to obtain a pure specimen of the nitro-base, the crude product was dissolved in methyl alcohol, mixed with ether, washed several times with water, the clear ethereal solution dried, concentrated, and diluted with petroleum (b. p. 40—60°) until a turbidity was produced. After some time the nitro-base separated in nodular masses of buff-coloured needles, m. p. 118° (Found : C, 61·8; H, 5·8. $C_{20}H_{22}O_6N_2$ requires C, 62·2; H, 5·7%). It is very soluble in the usual organic solvents with the exception of petroleum, and dissolves in dilute mineral acids to a pale yellow solution. When an acid solution of the base is reduced with zinc dust, the filtered solution gives an intense blue coloration with ferric chloride. The *hydriodide* is precipitated by the addition of potassium iodide to a solution of the base in dilute hydrochloric acid, and crystallises from much alcohol in pale yellow, elongated prisms, m. p. 213°. The *picrate* separates as an oil, which rapidly hardens, when an alcoholic solution of the base is treated with picric acid. It crystallises from glacial acetic acid in lemon-yellow needles, m. p. 192°.

6′-*Aminoveratrylhydrohydrastinine* (V).—6′-Nitroveratrylhydrohydrastinine (10 g.) was dissolved in glacial acetic acid (40 c.c.) and allowed to remain at 15° with hydrated stannous chloride (20 g.) and concentrated hydrochloric acid (40 c.c.) for 12 hours, when a crystalline tin double salt separated. The mixture was poured into water (500 c.c.), filtered, made strongly alkaline with potassium hydroxide, and extracted several times with chloroform; the extracts were dried over potassium carbonate and concentrated. The residual oil was very soluble in organic solvents with the exception of petroleum, and all attempts to induce crystallisation

have failed. The *dihydrochloride* was obtained by dissolving the base in ethyl alcohol and saturating with dry hydrogen chloride, when a mass of small, colourless prisms separated. These are sparingly soluble in methyl or ethyl alcohol, but readily soluble in water, the latter solution giving an intense blue coloration with ferric chloride. It recrystallises from aqueous alcohol in colourless prisms, m. p. 250° (decomp.) (Found : C, 56·1 ; H, 6·2. $C_{20}H_{26}O_4N_2Cl_2$ requires C, 55·9 ; H, 6·1%). The *base* was liberated from the hydrochloride by sodium hydroxide as a colourless, viscid oil.

dl-*Dicentrine* (VI).—The above dihydrochloride (2·5 g.) was dissolved in a little water, made alkaline with sodium hydroxide, and the base extracted with ether, dried, the solvent removed, and the residual oil dissolved in 10% sulphuric acid (10 c.c.). The solution was cooled by the addition of ice (20—30 g.) and 2*N*-sodium nitrite solution (3 c.c.) slowly added. The solution became emerald green and after ½ hour copper powder (1 g.) was added, when nitrogen was rapidly evolved and the solution developed a red coloration. After 3 hours the copper was removed by filtration, the filtrate reduced with zinc dust (1 g.) and concentrated hydrochloric acid (3 c.c.) and again filtered.

A second experiment was carried out on the same scale, and the slightly warm combined filtrates were extracted twice with chloroform. On cooling, *dl*-dicentrine hydrochloride (0·4 g.) separated from the chloroform whilst some non-basic resin remained dissolved. The acid liquors were made alkaline with ammonia and extracted six times with ether, the extracts dried with sodium sulphate, concentrated, and the residual oil was dissolved in boiling 15% hydrochloric acid (10 c.c.), filtered, and cooled, when a further crop of *dl*-dicentrine hydrochloride (0·5 g.) was obtained, the total yield being about 15% of that theoretically possible.

The other products of the reaction have not been closely investigated, but it might be mentioned that some phenolic base and probably also veratrylhydrohydrastinine are present in the dark-coloured hydrochloric acid liquors. Further a dark brown, amorphous substance is precipitated when the acid solution is rendered alkaline with ammonia, which is almost insoluble in ether and has not been further investigated.

dl-*Dicentrine* was obtained by dissolving the hydrochloride in boiling water, neutralising with sodium hydroxide, collecting the cream-coloured base, washing with water, and crystallising from methyl alcohol, when colourless prisms, m. p. 178—179°, were obtained (Found : C, 70·5 ; H, 6·2. $C_{20}H_{21}O_4N$ requires C, 70·8 ; H, 6·2%). It is readily soluble in chloroform, ethyl acetate, acetone, benzene, and hot alcohol, moderately soluble in ether and

cold alcohol, and sparingly soluble in petroleum. It dissolves in concentrated sulphuric acid to a colourless solution which rapidly becomes reddish-violet. A colourless solution is obtained with Erdmann's reagent which rapidly becomes greenish-blue, whilst deep blue colorations are developed immediately with Fröhde's and Mandelin's reagents. The *hydrochloride*, obtained by dissolving the base in hot dilute hydrochloric acid, is very sparingly soluble in alcohol and cold water, but crystallises from boiling water in a gelatinous mass or very small, colourless needles which darken at 250° and melt with some decomp. at 263—265° (Found: C, 63·3; H, 5·8. $C_{20}H_{22}O_4NCl$ requires C, 63·6; H, 5·8%). The *methiodide* was obtained by heating the base with a large excess of methyl iodide in a sealed tube at 100° for 1 hour. The methyl iodide was removed by distillation, and the residue extracted with boiling alcohol, from which the methiodide separated on cooling in well-defined, colourless, four-sided plates, m. p. 228—229° (Found: C, 52·7; H, 5·1. $C_{21}H_{24}O_4NI$ requires C, 52·4; H, 5·0%). The *picrate* was prepared in alcoholic solution and crystallised from much alcohol in orange prisms, m. p. 188—189°.

One of us (R. D. H.) is indebted to the Commissioners of the 1851 Exhibition for a studentship which has enabled him to take part in this research, and to the Research Fund Committee of the Chemical Society for a grant which has defrayed some of the expenses of the investigation.

THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, July 7th*, 1925.]

CCLXXIV.—*Aminobenzthiazoles. Part I.* 1-*Anilinobenzthiazole and its Tolyl Homologues.*

By ROBERT FERGUS HUNTER.

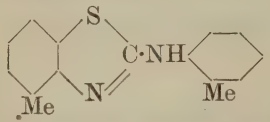
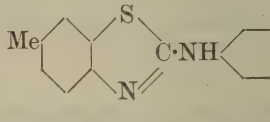
THE objects of this series of investigations are: to synthesise benzthiazoles and allied heterocyclic ring systems from arylthiocarbamides, to study the chemistry of the bromo-addition compounds of the aminobenzthiazoles, and to examine the mobility of the triad system N:C·N[H] $\rightleftharpoons$ N[H]·C:N in amino- and substituted aminothiazoles. The synthesis of 1-anilinobenzthiazole (I) from *s*-diphenylthiocarbamide by way of the tetrabromide of the former (Hugershoff, *Ber.*, 1903, **36**, 3121) probably takes place by way of a labile dibromo-addition compound of the thiocarbamide (*loc. cit.*). The thiazole must always be isolated as the tetrabromide and in a sense the ten-

dency to close the thiazole ring is dependent on the tendency to form the bromo-addition compound.

(I.) $C_6H_4<^{S}_{N}>C\cdot NHPh$ $C_6H_4<^{SBr_2}_{NBr_2}>C\cdot NHPh$ (II.)

The physical and chemical properties of 1-anilinobenzthiazole tetrabromide leave little doubt that the compound has a perbromide structure, probably (II) : it is reduced by sulphurous acid in the usual way (this vol., p. 1318) ; on treatment with alkalis, hydroxylic solvents, etc., it passes into dibromoanilinobenzthiazole ; and on exposure to air it gradually loses part of its bromine, yielding a stable tribromide.

Hugershoff (*loc. cit.*) observed that di-*o*- and -*p*-tolylthiocarbamides on bromination formed red bromides, which on reduction yielded " tolylaminotoluthiazoles " : these must be 1-*o*-toluidino-3-methylbenzthiazole (III) and 1-*p*-toluidino-5-methylbenzthiazole (IV), respectively.

(III.)   (IV.)

He did not, however, investigate the bromides beyond noting that they lost bromine on exposure to air, yielding yellow, crystalline substances.

The first product of bromination of di-*o*-tolylthiocarbamide in chloroform is the red unstable hexabromide (V), whilst di-*p*-tolylthiocarbamide yields a tetrabromide (VI). These lose bromine on exposure to air, yielding stable tribromides ; on reduction they are converted into the thiazoles (III and IV, respectively), and on treatment with hydroxylic solvents and alkalis pass into dibromo-1-toluidinomethylbenzthiazoles, $C_6H_2MeBr<^{S}_{N}>C\cdot NH\cdot C_7H_6Br$.

$C_6H_3Me<^{SBr_4}_{NBr_2}>C\cdot NH\cdot C_7H_7$ (V.) $C_6H_3Me<^{SBr_2}_{NBr_2}>C\cdot NH\cdot C_7H_7$ (VI.)

The tribromides resemble the higher bromides in regard to their ease of reduction by sulphurous acid and their conversion into dibromo-substitution products by alkalis, but differ markedly from them in stability. They all crystallise from inert solvents in well-defined crystals of definite melting point and are relatively stable to air. They are, further, incapable of conversion into the higher bromides by bromination.

The conversion of the higher bromides into the tribromides is a mild oxidative change involving the direct elimination of bromine.

In view of the stability of the products it appears reasonable to suggest that they are the hexabromides of condensation products, 1-anilinobenzthiazole tribromide, for example, being

(VII.) $Br_2N\ll\overset{C(NHPh)}{\underset{C_6H_4}{—}}\gg SBr\cdot SBr\ll\overset{C(NHPh)}{\underset{C_6H_4}{—}}\gg NBr_2$;

unfortunately, concordant values for the molecular weights have not yet been obtained.

To complete the present study, the bromination of di-*m*-tolylthiocarbamide has been investigated. A red, crystalline hydrobromide was isolated containing seven bromine atoms,

(VIII.) $C_6H_3Me\ll\overset{SBr_4}{NBr_2}\gg C\cdot NH\cdot C_7H_7,HBr$.

The compound yielded a yellow bromide on exposure to air, and on reduction passed into the free base, which may be either 1-*m*-toluidino-4- or -6-methylbenzthiazole. In the absence of definite proof of its structure, it is proposed to term it 1-m-*toluidino*-m-*toluthiazole*.

Experimental.

s-Di-*o*-, -*m*-, and -*p*-tolylthiocarbamides were prepared as described in the literature and melted at 161°, 112°, and 176°, respectively.

1-*Anilinobenzthiazole* (I).—*s*-Diphenylthiocarbamide (50 g.) suspended in 260 c.c. of chloroform was brominated according to Hugershoff's directions (*loc. cit.*). The red needles of the tetrabromide were dried in a vacuum [m. p. 112° (decomp.). Found : Br, 56·8. Calc., Br, 58·6%], suspended in sulphurous acid, and reduced with sulphur dioxide until all solid matter was colourless on crushing. The product was digested with warm 2*N*-sodium hydroxide, the free base washed, dried at 110° (yield quantitative), and crystallised first from ethyl acetate, which is a much better solvent than the alcohol recommended by Hugershoff, and then twice from absolute alcohol; it was thus obtained in small crystals, m. p. 159°. The *acetyl* derivative had m. p. 158° after recrystallisation from ethyl acetate.

The tetrabromide (II) was prepared by heating 1 g. of thiocarbanilide and 1 c.c. of bromine in chloroform under reflux for 2 minutes; on cooling and scratching, fine, red needles separated, which were dried in a vacuum over potassium hydroxide (Found : Br, 58·8%). The substance commences to decompose at about 110°, and melts at 117°. Hugershoff's m. p. of 136° is possibly given erroneously, since even the tribromide melts more than 10° below this temperature.

1-*Anilinobenzthiazole Tribromide* (VII ?).—Bromine was gradually

evolved when 5 g. of the tetrabromide were exposed to the atmosphere for 2 or 3 days. The yellow, crystalline product, m. p. usually about 115°, was recrystallised from chloroform, the *tribromide* being obtained in small, yellow prisms which sintered at about 120° and melted to a clear red liquid at 125° (Found : Br, 51·5. $C_{13}H_{10}N_2Br_3S$ requires Br, 51·7%).

1-o-*Toluidino*-3-*methylbenzthiazole* (III).—Di-*o*-tolylthiocarbamide (10 g.) dissolved in 50 c.c. of chloroform was brominated with 8·5 c.c. of bromine, diluted with an equal volume of chloroform, as in the previous case. The solution, after being heated under reflux for 10 minutes, was either agitated with " dry " ether, when the tribromide of the thiazole separated, or evaporated in a vacuum at room temperature, when a red crystalline crust of a mixture of bromides was obtained; this became yellow at 187°, brown at 205°, red at 230°, viscous and dark at 260°, and melted with charring at 265°. The crude bromide obtained by either method was reduced as in the previous case, and the product was boiled with 2*N*-alkali for a short time. The free base melted below the liquid and hardened on cooling; after being washed and dried, it was crystallised from ethyl acetate, and then from alcohol, being thus obtained in short prisms, m. p. 135° (sintering).

The *acetyl* derivative was obtained in minute crystals sintering at 77°.

1-o-*Toluidino*-3-*methylbenzthiazole Hexabromide* (V).—Di-*o*-tolylthiocarbamide (1 g.) was brominated as in the previous case, and the solution, after being heated under reflux for 3 minutes, was cooled; the fine, red needles of the hexabromide which separated on scratching were dried in a vacuum over potassium hydroxide. They lost bromine at 60° and melted to a clear red liquid at 76—78° (Found : Br, 66·4. $C_{15}H_{14}N_2Br_6S$ requires Br, 65·5%).

The *tribromide* was obtained by exposing 5 g. of the red bromide to the air as in the previous case. After recrystallisation from chloroform it was obtained in small, yellow, glistening prisms, m. p. 250° (decomp.), becoming orange at 205° and red-brown at 240° [Found : Br, 48·7. $(C_{15}H_{14}N_2Br_3S)_2$ requires Br, 48·6%].

Dibromo-1-o-*toluidino*-3-*methylbenzthiazole*.—When boiled with alcohol, either bromide dissolved; thereafter colourless crystals of the *hydrobromide* of the dibromo-substitution product suddenly separated. These, recrystallised from glacial acetic acid and washed with ether, were obtained in lustrous prisms, m. p. 280° (decomp.) (Found : Br, 48·0. $C_{15}H_{12}N_2Br_2S,HBr$ requires Br, 48·7%). The hydrobromide was digested with warm 2*N*-sodium hydroxide, and the free base was recrystallised from glacial acetic acid and washed with ether; tufts of shining needles, m. p. 205°, were obtained, which

however, retained an appreciable quantity of acetic acid (Found : Br, 32·9%). They were digested with warm alcohol; the base was then obtained in small prisms having the same m. p. as before (Found : Br, 39·3. $C_{15}H_{12}N_2Br_2S$ requires Br, 38·9%).

1-p-*Toluidino*-5-*methylbenzthiazole* (IV).—Di-*p*-tolylthiocarbamide (10 g.) was brominated as in the previous case. The red needles of the tetrabromide were dried in a vacuum and reduced. The free base crystallised from ethyl acetate in hair-like crystals, m. p. 162°.

The *acetyl* derivative was obtained in spherical aggregates of needles, m. p. 158°. The *tetrabromide*, prepared as in the previous case, sintered at 130°, softened at 140°, and melted to a clear red liquid at 145° (Found : Br, 54·9. $C_{15}H_{14}N_2Br_4S$ requires Br, 55·6%). The *tribromide*, obtained by exposing the tetrabromide to the air for some days, crystallised from chloroform in slender, orange needles softening at 145°; m. p. 148° (decomp.) [Found : Br, 49·2. $(C_{15}H_{14}N_2Br_3S)_2$ requires Br, 48·6%].

Dibromo-1-p-*toluidino*-5-*methylbenzthiazole*.—The tribromide was dissolved in boiling alcohol, and the solution concentrated; on scratching and cooling, the *hydrobromide* separated. After recrystallisation from glacial acetic acid it was obtained in small crystals turning yellow at 220°, pale brown at 240°, and melting at 256—258° (Found : Br, 47·8. $C_{15}H_{13}N_2Br_3S$ requires Br, 48·7%). It was treated with warm dilute alkali, and the free base recrystallised from glacial acetic acid and washed with ether, when pale cream crystals were obtained, m. p. 159—160°. They retained an appreciable quantity of solvent as in the case of the *o*-compound (Found : Br, 36·6. $C_{15}H_{12}N_2Br_2S$ requires Br, 38·9%).

1-m-*Toluidino*-m-*toluthiazole*.—Di-*m*-tolylthiocarbamide (4 g.) was dissolved in 40 c.c. of chloroform and brominated with 6 c.c. of bromine diluted with an equal volume of chloroform; heat and hydrogen bromide were evolved and the red bromide was crystalline. The product was dried in a vacuum and reduced by sulphurous acid and sulphur dioxide in the usual way. The base crystallised from ethyl acetate in small, stout, colourless crystals, m. p. 184—186° (Found : S, 11·7. $C_{15}H_{14}N_2S$ requires S, 12·6%).

1-m-*Toluidino*-m-*toluthiazole Hexabromide Hydrobromide*.—Di-*m*-tolylthiocarbamide (1 g.) was dissolved in chloroform and brominated with 1 c.c. of bromine, the solution was refluxed for 3 minutes and allowed to cool slowly in a hot water-bath; the small, four-sided, red tablets which separated were dried in a vacuum over potassium hydroxide. They crumbled to a semi-crystalline, dark mass at 110°, became orange and crystalline at 187°, pale yellow at 197°, and were unmelted above 200° (Found : Br, 69·1. $C_{15}H_{15}N_2Br_7S$ requires Br, 68·9%).

1-m-*Toluidino*-m-*toluthiazole Tribromide Hydrobromide*.—The red bromide was exposed to the atmosphere for some days, and the orange-yellow crystalline residue refluxed with chloroform, in which it was very sparingly soluble. The product consisted of small, yellow crystals of the usual type which softened at 136° and sintered at 190° [Found: Br, 56·3. $(C_{15}H_{15}N_2Br_4S)_2$ requires Br, 55·6%].

The bromide was reduced in the usual way by sulphurous acid and showed the usual stability to air, etc.

In conclusion, the author desires to express his gratitude to Prof. J. F. Thorpe, F.R.S., for the kind interest he has taken in the progress of these experiments.

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CCLXXV.—*The Amino-4-Pyridones.*

By WILLIAM HAUGHTON CROWE.

A COMPARISON of the reactions of the pyridones with those of the aromatic phenols is of considerable interest, and in connexion with the formation of nitro-derivatives and their subsequent reduction it has already been shown that 4 : 6-dimethyl-2-pyridone (Collie and Tickle, J., 1898, **73**, 229) and lutidone (Collie and Hall, J., 1898, **73**, 237) exhibit a formal resemblance to the corresponding xylenols. The simplest pyridones are not very readily accessible and this circumstance no doubt accounts for the fact that their substitution products have not been closely studied. A mononitro-4-pyridone, m. p. 279°, and a dinitro-4-pyridone have now been obtained and reduced; the former by tin and hydrochloric acid to an amino-4-pyridone, and the latter by ammonium sulphide to an aminonitro-4-pyridone. Whilst the work was in progress Koenigs and Freter (*Ber.*, 1924, **57**, 1187) published an account of the nitration of 4-pyridone, but it appears that they did not isolate the nitro-derivatives in a pure condition. Thus they state that the mononitro-derivative has m. p. 269—270° and that the yellow dinitro-compound crystallises with $1H_2O$.

EXPERIMENTAL.

3-*Nitro*-4-*pyridone*.—A mixture of 4-pyridone, fuming nitric acid, and concentrated sulphuric acid was heated on the water-bath for 2 days, poured into water, the acid nearly neutralised with solid sodium carbonate, the solution evaporated to dryness, and the residue extracted with alcohol. The product crystallised from hot

water in yellow needles, m. p. 279° (Found : C, 43·0; H, 3·9; N, 20·2. $C_5H_4O_3N_2$ requires C, 42·9; H, 2·9; N, 20·0%). A concentrated solution gave a lemon-yellow precipitate of the sodium salt on treatment with sodium hydroxide.

3-*Amino*-4-*pyridone*.—Reduction of the nitro-compound with tin and hydrochloric acid proceeded very violently. The solution was diluted with water, the tin removed as sulphide, and the filtrate evaporated on the water-bath; the crystals of the *hydrochloride* thus obtained were dried in a vacuum over sulphuric acid (Found : Cl, 22·0. $C_5H_6ON_2,HCl,H_2O$ requires Cl, 21·6%). The *chloroplatinate* was obtained by treating a concentrated solution of the hydrochloride with platinic chloride and crystallised from hot concentrated hydrochloric acid [Found : C, 18·3; H, 2·5; Pt, 30·1. $(C_5H_6ON_2)_2,H_2PtCl_6,H_2O$ requires C, 18·5; H, 2·5; Pt, 30·1%].

3 : 5-*Dinitro*-4-*pyridone*.—A mixture of 4-pyridone (2 g.), fuming nitric acid (7 c.c.), and concentrated sulphuric acid (13 c.c.) was heated at 140° for about 8 hours and poured into cold water, when 3 : 5-*dinitro*-4-*pyridone* was obtained as a faintly yellow, crystalline precipitate. It crystallised from 50% acetic acid in long, colourless needles (Found : N, 22·9. $C_5H_3O_5N_3$ requires N, 22·7%). A solution in alcohol and acetone gave with sodium ethoxide a brilliant yellow precipitate of the sodium salt.

3-*Nitro*-5-*amino*-4-*pyridone*.—The dinitropyridone was boiled under reflux with the calculated quantity of ammonium sulphide in alcohol, the solid filtered off, and extracted with hot strong hydrochloric acid. On cooling, the *hydrochloride* crystallised in needles, which were recrystallised from concentrated hydrochloric acid with the addition of animal charcoal (Found : C, 31·7; H, 3·5; N, 22·1; Cl, 18·3. $C_5H_5O_3N_3,HCl$ requires C, 31·4; H, 3·7; N, 21·9; Cl, 18·5%). The substance gave yellow solutions, and turned orange in the air, due to loss of hydrogen chloride and formation of the free base.

The author wishes to express his indebtedness to Professor J. N. Collie, F.R.S., for his valuable help and advice during the research, and also to the Department of Scientific and Industrial Research for a grant which made the work possible.

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University College, London. [*Received, April 13th*, 1925.]

CCLXXVI.—*Researches on Residual Affinity and Co-ordination. Part XXV. A Quadridentate Group Contributing Four Associating Units to Metallic Complexes.*

By Gilbert T. Morgan and J. D. Main Smith.

Fundamental advances were made in the experimental verification of the co-ordination theory when Werner showed that certain compounds and compound radicals were capable of furnishing two associating units to the co-ordination complex surrounding a metallic atom, for by means of such complexes he was able to identify the three-dimensional structure of many co-ordination compounds. Of chemical substances contributing two associating units the following may be cited: ethylenediamine, αα-dipyridyl, dimethyldithiolethylene, and tetramminodihydroxycobaltic bromide, $(NH_3)_4Co(OH)_2Br$, the last of these being noteworthy owing to its completely inorganic character. There are also numerous complex radicals which function as two associating units: the carbonato-, malonato-, and oxalato-groups and the monoenolic radicals of acetylacetone and its homologues, R·CO·CH:C(OH)R′, R and R′ being alkyl or aryl groups. To these compounds and compound radicals capable of occupying two positions in the co-ordination complex the generic name of chelate groups has been given (J., 1920, **117**, 1457) because their tenacious grip of the implicated metallic atom leads to the formation of remarkably stable co-ordination complexes.

Werner also identified groups capable of treble attachment to metallic atoms, such tridentate residues containing three fused chelate groups. The tridentate groups recognised by Werner already contained, however, one metallic atom, so that on association of these tridentate groups with the co-ordinating nuclear atoms the complexes became binuclear, as, for instance, in the case of triamminocobaltic hydroxide, $(NH_3)_3Co(OH)_3$, identified in the complex cation of the salt in which the three hydroxyl groups

$$\left[\begin{matrix} & OH & \\ (NH_3)_3Co & OH & Co(NH_3)_3 \\ & OH & \end{matrix}\right] Br_3$$

contribute simultaneously three units to the co-ordination numbers of each of two cobalt atoms.

Recently Pope and Mann have proved that αβγ-triaminopropane, $NH_2·CH_2·CH(NH_2)·CH_2·NH_2$, is capable of treble attachment to metallic atoms. Two molecular proportions of this triacidic base

(*tp*) occupy six co-ordination positions round cobalt and rhodium atoms, forming the complex cations $[Co\ tp_2]'''$ and $[Rh\ tp_2]'''$. This demonstration constitutes the first example of a tridentate non-metallic group in complexes containing a single nuclear atom (*Compt. rend.*, 1924, **178**, 2085; *Proc. Roy. Soc.*, 1925, **107**, 80).

We have now succeeded in identifying a group capable of quadruple attachment to metallic atoms, this being the first known case of a quadridentate group in co-ordination complexes. This quadridentate group is furnished by the bivalent radical of *ethylenediaminobisacetylacetone*, $C_{12}H_{20}O_2N_2$, a compound first prepared by Combes (*Compt. rend.*, 1889, **108**, 1252) on condensing two molecules of acetylacetone with one molecule of ethylenediamine with elimination of two mols. of water. Combes showed that this product is a dienolic diketone,

$CH_3{\cdot}C(OH){:}CH{\cdot}C(CH_3){:}N{\cdot}CH_2{\cdot}CH_2{\cdot}N{:}C(CH_3){\cdot}CH{:}C(OH){\cdot}CH_3$,

yielding a violet cupric salt containing one atomic proportion of copper to one molecular proportion of the dienolic radical.

In attempting to prepare an additive co-ordination compound of cupric acetylacetone and ethylenediamine we obtained accidentally the green monohydrate of Combes's violet salt, copper ethylenediaminobisacetylacetone, which separated from the indigo-blue solution of copper acetylacetone in ethylenediamine hydrate. This observation led to other experiments on Combes's ethylenediaminobisacetylacetone and particularly to the preparation of its *cobaltous* salt,* a non-ionised complex which proved to be dihydrated, and,

$$\left[(H_2O)_2\ Co^{II}\begin{matrix}O\\N\\N\\O\end{matrix}\right\}C_{12}H_{18}\right] \qquad \text{(I.)}$$

as the co-ordination number of bivalent cobalt is usually six, this composition suggested that the organic group might occupy four of the six co-ordination positions. Since, however, the co-ordination number of tervalent cobalt is invariably six, the oxidation of this cobaltous salt in the presence of ammonia should, on the foregoing supposition, lead to a cobaltammine containing two of ammonia and one molecular proportion of the supposed quadridentate group per cobaltic atom with a single univalent acidic ion outside the complex.

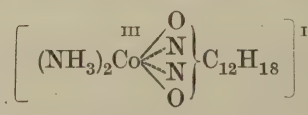
On reaction with ammonium chloride, excess of ammonia, and hydrogen peroxide, this supposition was verified, for the cobaltous salt yielded the anticipated cobaltammine readily and almost

* The co-ordination compounds of ethylenediaminobisacetylacetone with several other bivalent metals have been investigated and will be discussed subsequently.

quantitatively. The chloride radical present was wholly ionised, immediately precipitable with silver nitrate, and yielded the less soluble *bromide*, *iodide*, *chlorate*, *perchlorate*, *nitrite*, *nitrate*, and d-*camphorsulphonate* (Reychler) by double decomposition with the sodium or potassium salts of the corresponding acids.

Excepting the chloride and *d*-camphorsulphonate, all the salts prepared were anhydrous when crystallised from water, thus confirming the view that the cobaltic co-ordination number of six is made up solely of two ammonia molecules and the organic radical. Hence this organic radical, which contributes four to the cobaltic co-ordination number, is actually a quadridentate group.

The univalent complex cobaltammine ion is thus demonstrated to have the following chemical constitution :



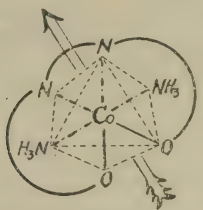
Five stereochemical arrangements of the groups present in this co-ordination complex are, however, possible, depending on the positions taken up on the octahedron by the ammonia molecules and by the bivalent quadridentate group, $C_{12}H_{18}N_2O_2$ or

$$-O\cdot C(CH_3){:}CH\cdot C(CH_3){:}N\cdot CH_2\cdot CH_2\cdot N{:}C(CH_3)\cdot CH{:}C(CH_3)\cdot O-.$$

If the two ammonia molecules are in the antipodal *trans*-positions (Diagram 1) the quadridentate group must be wrapped equatorially round the octahedron. This configuration contains two planes of symmetry and the compound is optically inactive and irresolvable. If the two ammonia molecules are in contiguous *cis*-positions, then three associating units of the quadridentate group must occupy the corners of one triangular face of the octahedron with the fourth associating unit overlapping on to an adjacent face, and this arrangement can be made in four different ways, giving rise to four stereoisomeric modifications. None of these four isomerides possesses a plane, a centre, or an alternating axis of symmetry and hence they are all optically active. Two of them are mirror images of the other two and the four isomerides comprise two enantiomorphous pairs.

Conclusive evidence has now been obtained that the product actually isolated contains two racemoid modifications which have been resolved into optically active forms by *d*-camphorsulphonic (Reychler) acid, and that all these active forms on keeping are spontaneously transformed into the single inactive and irresolvable form. The lack of optical activity in the last indicates that it is the *trans*-form (Diagram 1), in which the pair of ammonia molecules is in the *trans*-octahedral position. The active form with the low optical activity is in all probability the *cis-trans*-form (Diagram 2),

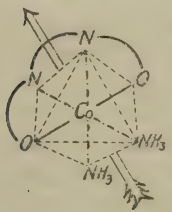
in which only the dyad axis of symmetry of the *trans*-form is retained, the pair of ammonia molecules here being in the *cis*-position while the pair of oxygen atoms is retained in the *trans*-position. The active form with the very high activity may thus be regarded as the *cis*-form (Diagram 3), in which none of the elements of symmetry is retained, the pair of oxygen atoms as well as the pair of ammonia molecules being in *cis*-positions.



Two Planes of Symmetry intersecting in One Dyad Axis of Symmetry.

Diagram 1.

Trans Inactive Isomeride



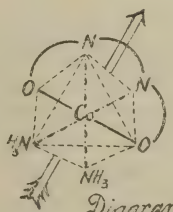
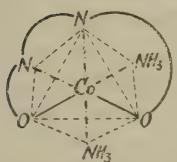
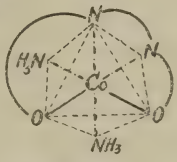


Diagram 2.

Cis-trans Enantiomorphous Pair each with One Dyad Axis of Symmetry and small optical activity.





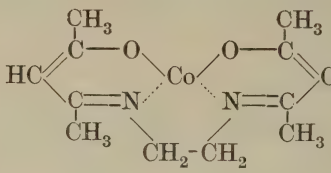
Cis-cis Enantiomorphous Pair without elements of Symmetry and with high optical activity

Diagram 3.

It has not been possible, however, to confirm these structures by chemical means, for the compounds are not decomposed by hot concentrated hydrochloric or hydrobromic acid to yield either the *cis* (violeo)- or *trans* (praseo)-dichlorodiamminoethylenediamminocobaltic halides which could be identified by their respective violet and green colours.

Whatever be the exact chemical structure of the organic group in the complex, the evidence is conclusive that it is a quadridentate

group and moreover that it can be arranged spatially round the co-ordination sphere so as to yield the *cis*- and *trans*-configurations with respect to the ammonia molecules (Diagrams 1, 2 and 3). The tricyclic system of the three chelate components of the quadridentate group associated with the octahedral cobalt atom is shown in plan in Diagram 4; two of the rings are six-membered and one is five-membered.



(*Diagram* 4.)

Experimental.

$C_2H_4(N{:}C{\cdot}CH_3{\cdot}CH{\cdot}CO{\cdot}CH_3)_2$ = ec (ethylenediaminobisacetylacetone).

*Diaquocobaltous Ethylenediamino*bis*acetylacetone*, $[(H_2O)_2\,ec\,Co]$ (Formula I).—Hexa-aquocobaltous chloride (4·8 g. = 1 mol.) was dissolved in hot water (20 c.c.), and ethylenediaminobisacetylacetone (4·5 g. = 1 mol.) and 5*N*-sodium hydroxide (8 c.c. = 2 mols.) added, forming a green paste. On boiling, the mixture turned brownish-yellow and a reddish-orange, crystalline precipitate separated. After washing with water and air-drying, bright orange-red prisms were obtained in yield varying from 85 to 45%, the higher yields being obtained with exclusion of air during the reaction (Found: Co, 18·7. $C_{12}H_{22}O_4N_2Co$ requires Co, 18·6%). The compound was insoluble in water and readily dissolved in most organic solvents to orange solutions which darkened in air owing to oxidation. It readily dissolved in dilute mineral acids with complete decomposition into acetylacetone and cobaltous and ethylenediamine salts.

*Diamminoethylenediamino*bis*acetylacetonocobaltic Chloride Dihydrate*, $[(NH_3)_2Coec]Cl(H_2O)_2$.—This salt was readily obtained in 83% yield on oxidation of the foregoing cobaltous salt by the calculated amount of 6*N*-hydrogen peroxide in the presence of excess of 18*N*-ammonia and ammonium chloride. The salt separated from the cooled mixture in pale fawn needles which were recrystallised from hot water, washed with alcohol, and air dried [Found: Co, 15·2; N (as NH_3), 7·35; H_2O, 8·1. $C_{12}H_{28}O_4N_4ClCo$ requires Co, 15·3; N (as NH_3), 7·25; $2H_2O$, 9·3%).

This feebly coloured cobaltic salt was moderately soluble in water to a brownish-red, neutral solution, from which silver nitrate solution immediately precipitated silver chloride. Concentrated solutions of the appropriate sodium or potassium salts precipitated

the bromide, iodide, nitrite, nitrate, chlorate, perchlorate, and *d*-camphorsulphonate of the complex base from concentrated solutions of the chloride. The chloride dissolved in boiling concentrated hydrochloric or hydrobromic acid solutions, but was not decomposed. It dissolved in boiling caustic soda solution, evolving ammonia and forming a clear reddish-brown solution which appeared to contain the complex diaquo-base. The chloride was quite insoluble in all organic solvents.

The following salts were prepared in quantitative yield by precipitation from concentrated solutions of the chloride by concentrated solutions of the appropriate alkali salt. All except the *d*-camphorsulphonate (Reychler) were very sparingly soluble in water and were precipitated as fine, yellowish-brown needles, which were washed with water and alcohol and air-dried. The camphorsulphonate, which is moderately soluble in water and in moist alcohol, was recrystallised from water and washed with acetone and ether and air-dried.

Bromide, $[(NH_3)_2$ ec Co]Br. Found: Co, 14·7; H_2O at 100°, nil. $C_{12}H_{24}O_2N_4BrCo$ requires Co, 14·9%.

Iodide, $[(NH_3)_2$ ec Co]I. Found: Co, 13·4; N (as NH_3), 6·4; H_2O at 100°, nil. $C_{12}H_{24}O_2N_4ICo$ requires Co, 13·4; N (as NH_3), 6·3%.

Nitrite, $[(NH_3)_2$ ec Co]NO_2. Found: Co, 16·2; N (as NH_3), 7·8; N (as NO_2), 4·0; organic N, 7·6; C, 39·7; H, 6·6; H_2O at 100°, nil. $C_{12}H_{24}O_4N_5Co$ requires Co, 16·3; N (as NH_3), 7·8; N (as NO_2), 3·9; organic N, 7·8; C, 39·9; H, 6·65%.

Nitrate, $[(NH_3)_2$ ec Co]NO_3. Found: Co, 15·7; H_2O at 100°, nil. $C_{12}H_{24}O_5N_5Co$ requires Co, 15·7%).

Chlorate, $[(NH_3)_2$ ec Co]ClO_3. Found: Co, 14·8; H_2O at 100°, nil. $C_{12}H_{24}O_5N_4ClCo$ requires Co, 14·8%.

Perchlorate, $[(NH_3)_2$ ec Co]ClO_4. Found: Co, 14·2; H_2O at 100°, nil. $C_{12}H_{24}O_6N_4ClCo$ requires Co, 14·2%.

d-*Camphorsulphonate*, $[(NH_3)_2$ ec Co]$C_{10}H_{15}O_4S,H_2O$. Found: Co, 10·6; H_2O at 100°, 3·1. $C_{22}H_{41}O_7N_4SCo$ requires Co, 10·6; H_2O, 3·2%.

Resolution of the Racemoid Mixture.—Aqueous solutions of the salts were transparent only in the darker red of the spectrum, and the light of the lithium line 6708 Å. (10^{-8} cm.) was used throughout the polarimetric measurements. Owing to the intensity of colour, solutions stronger than about 1% of the camphorsulphonates and 0·5% of the bromides in 0·5-dcm. tubes could not be used.

cis-dextro-*Bromide*.—On mixing saturated solutions of the complex chloride and the sodium salt of *d*-camphorsulphonic (Reychler) acid, fine, pale fawn needles of the *d*-camphorsulphonate separated,

isolated in six crops, which were washed with acetone and ether and air-dried. The first crop was found to be strongly dextrorotatory. The second crop was redissolved in water and decomposed with a solution of potassium bromide, the complex bromide immediately separating in fine, fawn needles, which were washed with alcohol and ether and air-dried (Found : Co, 14·7%). This bromide was indistinguishable in appearance and general properties from the racemoid bromide, but was strongly dextrorotatory, $[\alpha]_{Li} = +452°$, $[M] = +1784°$. Owing to the evanescent nature of this optical activity it was very fortunate that the specimens were submitted to independent observers.*

cis-trans-dextro-dextro-*Camphorsulphonate*.—The third crop from the above resolution had $[\alpha]_{Li} = +36°$, $[M] = +202·0°$, and deducting $+51·7°$ for the *d*-camphorsulphonate ion, $[M] = +150·3°$ for the cobaltic ion (Found : Co, 19·6%). Subsequent crops possessed successively diminishing activities. Recrystallisation of the crops failed to raise the activity for the cobaltic ion above $[M] = +150°$, and the most soluble crops invariably had a strong lævorotation. The highest lævorotation ever observed was $[M] = -108°$ for the cobaltic ion.

cis-trans-dextro-*Bromide*.—The corresponding *cis-trans-d-d*-camphorsulphonate was decomposed with potassium bromide solution, and the bromide isolated as in the case of the *cis*-bromide (Found : Co, 14·8%). $[\alpha]_{Li} = +40°$, $[M] = +158°$. This *cis-trans*-bromide alone was invariably obtained after the first preparation, and was indistinguishable, except for optical activity, from the racemoid bromide.

Inactive (*or* trans) *Bromide*.—The foregoing optically active salts, on keeping a few days, were found to be completely inactive, the camphorsulphonates having only the activity due to the camphorsulphonate ion, and being irresolvable. Once these inactive salts had been identified, it was found impossible to prepare active salts again. Numerous preparations were performed at ordinary and low temperatures, in sunlight and in darkness, and even in new apparatus in a different building, but optically active salts were never again obtainable. A specimen of the first preparation, which had originally yielded both the *cis*- and the *cis-trans*-bromides, was found to be quite irresolvable after 10 days. We

* A specimen of the racemoid bromide (S. 2) and of the *cis*-bromide (S. 1) was submitted to Mr. C. E. Wood for polarimetric examination without informing him which or if either of the specimens was optically active. His report is as follows : *S*. 1.—Weight, 0·0664 g., dissolved in 12·5 c.c. of water and examined in 0·5-dcm. tube with light of lithium line 6708 Å., $[\alpha]_{Li} = +531°$, $[M] = +2097·4°$. *S*. 2.—Weight, 0·0666 g., dissolved in 12·5 c.c. of water and examined in 0·5-dcm. tube—inactive.—C. E. W.

are unable to assign the precise cause of the inability to obtain active salts after the first ten or so preparations, but it is worthy of remark that active salts could not be obtained after the inactive salts had been brought into existence, pointing to the probability that the result is due to infection. This possibility is not wholly ruled out by preparation in new apparatus in a different building, because the inactive salt may have been a partial product only in later preparations and the active salts simultaneously formed thus infected at the moment of coming into existence. Found for the inactive *bromide* : Co, 14·8%. The inactive bromide was indistinguishable in appearance and general properties from the racemoid and active bromides.

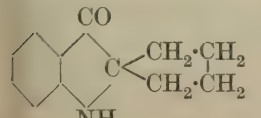
The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research for grants which have helped to defray the expense of this investigation.

UNIVERSITY OF BIRMINGHAM,
EDGBASTON. [*Received, July 15th,* 1925.]

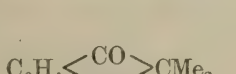
CCLXXVII.—*The Synthesis and Reactions of* 1-*Anilino*-cyclo*pentane*-1-*carboxylic Acid.*

By SYDNEY GLENN PRESTON PLANT and JOHN ERNEST FACER.

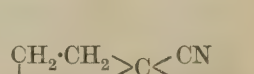
DURING the investigations of the derivatives of tetrahydrocarbazole (Perkin and Plant, J., 1921, **119**, 1825; 1923, **123**, 676) a substance (m. p. 113°) was isolated which appeared to be ψ-indoxyl*spirocyclo*pentane (I). Bucherer and Grolée (*Ber.*, 1906, **39**, 986) have prepared α-anilino*iso*butyric acid (see also Tiemann, *Ber.*, 1882, **15**, 2039; Bischoff and Mintz, *Ber.*, 1892, **25**, 2326) by the hydrolysis of the nitrile obtained from the condensation of aniline with acetone cyanohydrin, and found that it could be made to give very small quantities of 2 : 2-dimethyl-ψ-indoxyl (II) on fusion with a mixture of sodium ethoxide and potassium hydroxide. A similar series of reactions, starting from aniline and *cyclo*pentanone cyanohydrin, ought to yield ψ-indoxyl*spirocyclo*pentane and so establish definitely the constitution of this product, from which several derivatives have been obtained (see also Sidgwick and Plant, this vol., p. 209).



(I.)

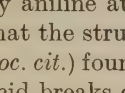


(II.)

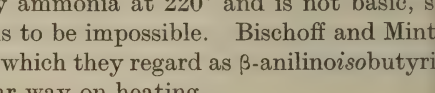


(III.)

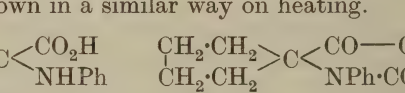
We have now prepared 1-*anilino*-1-*cyano*cyclo*pentane* (III) in this way and converted it into the corresponding *amide*, which can then be hydrolysed to 1-*anilino*cyclo*pentane*-1-*carboxylic acid* (IV). This acid is comparatively unstable and when heated above its melting point loses aniline and water, a substance (m. p. 142°) being formed which appears to be the lactone of 1-1′-*hydroxy*cyclo*pentane*-1′-*carboxylylanilino*cyclo*pentane*-1-*carboxylic acid* (V). This compound is slowly dissolved by a cold solution of sodium hydroxide and is slowly reprecipitated by hydrochloric acid. It is unchanged by aniline at 170° or by dry ammonia at 220° and is not basic, so that the structure (VI) seems to be impossible. Bischoff and Mintz (*loc. cit.*) found that the acid which they regard as β-anilino*iso*butyric acid breaks down in a similar way on heating.



(IV.)



(V.)



(VI.)

Fusion of 1-anilino*cyclo*pentane-1-carboxylic acid with a mixture of sodium ethoxide and potassium hydroxide gave no ψ-indoxyl-*spirocyclo*pentane, but considerable quantities of carbazole were isolated. Many different methods have been investigated for the purpose of eliminating water from the acid at a lower temperature, but without success. The acetyl derivative of 1-anilino*cyclo*pentane-1-carboxylic acid has also been prepared, but this resisted all efforts made to convert it into 6-acetyl-ψ-indoxyl*spirocyclo*pentane.

Experimental.

1-*Anilino*-1-*cyano*cyclo*pentane*.—The bisulphite compound (104 g.) of *cyclo*pentanone was added to water (300 c.c.) and treated with potassium cyanide (38 g.). The *cyclo*pentanone cyanohydrin was extracted with benzene, the solution washed with water and dried over calcium chloride. After the addition of aniline (50 g.), the mixture was boiled for 12 hours and then extracted with half its volume of dilute hydrochloric acid, washed with water, and the solvent removed under diminished pressure. The residue was dissolved in hot petroleum (b. p. 60—80°) and crude 1-*anilino*-1-*cyano*cyclo*pentane* separated, on cooling, as an oil which soon solidified. It was recrystallised from a small quantity of alcohol and obtained in colourless prisms, m. p. 58° (Found: C, 77·5; H, 7·5; N, 15·0. $C_{12}H_{14}N_2$ requires C, 77·5; H, 7·5; N, 15·0%). It decomposes on distillation with the formation of some aniline.

A solution of 1-anilino-1-cyano*cyclo*pentane in cold sulphuric acid

was kept for 2 days and then poured on to ice. On making alkaline with ammonia, the *amide* of 1-*anilino*cyclo*pentane*-1-*carboxylic acid* was precipitated in a pure condition. It separates from alcohol in colourless plates, m. p. 161° (Found : N, 13·5. $C_{12}H_{16}ON_2$ requires N, 13·7%). The *nitrosoamine*, precipitated on addition of sodium nitrite to a solution of the amide in dilute sulphuric acid, separates from alcohol in practically colourless prisms, m. p. 122° (Found : N, 18·0. $C_{12}H_{15}O_2N_3$ requires N, 18·0%).

1-*Anilino*cyclo*pentane*-1-*carboxylic Acid.*—The amide of the acid was dissolved in cold, concentrated hydrochloric acid and almost immediately a precipitate of the hydrochloride separated. The mixture was carefully evaporated to dryness and the residue treated with sodium hydroxide solution till alkaline. After boiling for a short time, the whole was filtered while still hot, and the filtrate acidified with acetic acid, when 1-*anilino*cyclo*pentane*-1-*carboxylic acid* separated as a colourless solid. It crystallised from xylene in colourless prisms, m. p. 162° (Found : N, 6·9. $C_{12}H_{15}O_2N$ requires N, 6·8%).

1-Anilino*cyclo*pentane-1-carboxylic acid is soluble in both acids and alkalis and gives a *nitrosoamine* which can be recrystallised from dilute alcohol and obtained in colourless plates, m. p. 124° (decomp.) (Found : N, 12·2. $C_{12}H_{14}O_3N_2$ requires N, 12·0%).

1-Anilino*cyclo*pentane-1-carboxylic acid, on heating at 230° in a small distillation flask, decomposes and a mixture of aniline and water can be collected. The residue solidifies on cooling, and can be purified by warming first with dilute hydrochloric acid and then with dilute sodium carbonate solution. On recrystallisation from petroleum, the *lactone* of 1-1′-*hydroxy*cyclo*pentane*-1′-*carboxylyl*-*anilino*cyclo*pentane*-1-*carboxylic acid* separates in clusters of colourless prisms, m. p. 142° (Found : C, 72·3; H, 7·3; N, 4·7. $C_{18}H_{21}O_3N$ requires C, 72·2; H, 7·0; N, 4·7%).

An intimate mixture of 1-anilino*cyclo*pentane-1-carboxylic acid (16 g.), sodium ethoxide (48 g.), and potassium hydroxide (40 g.) was gradually heated from 270° to 320° and maintained there for 15 minutes. After cooling, the product was pulverised and added to much water. The undissolved solid was collected, dried, and distilled. The colourless distillate (3 g.), which solidified, crystallised from alcohol in colourless plates, m. p. 238°, of carbazole, identified by analysis (Found : N, 8·5. Calc., N, 8·4%), a mixed melting point determination, and preparation of the picrate, which separated from alcohol in bright red needles, m. p. 184° (compare Schmidt and Schall, *Ber.*, 1907, **40**, 3230).

A solution of 1-anilino*cyclo*pentane-1-carboxylic acid (4 g.) in dry benzene (60 c.c.) was boiled with acetic anhydride (5 c.c.) for

7 hours, the benzene removed under reduced pressure, and the residue treated with acetone–petroleum. 1-*Acetylanilino*cyclopentane-1-*carboxylic acid* crystallises from acetone in colourless prisms, m. p. 195° (Found: N, 5·7. $C_{14}H_{17}O_3N$ requires N, 5·7%).

One of us (S. G. P. P.) wishes gratefully to acknowledge the receipt of a grant from the Chemical Society Research Fund which has defrayed a part of the cost of this investigation.

THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, June 30th,* 1925.]

CCLXXVIII.—*The Action of Nitrogen Dioxide on Anthracene Derivatives.*

By EDWARD DE BARRY BARNETT.

MEISENHEIMER (*Annalen*, 1902, **323**, 205; 1904, **330**, 133) has shown that treatment of anthracene and of 9-nitroanthracene with nitrogen dioxide leads to the addition of nitro-groups to the "bridge" bond with production of dinitro- and trinitro-dihydroanthracene. The action of alkali on these compounds leads to loss of 1 mol. of nitrous acid with re-establishment of the "bridge," but for this purpose pyridine is much more satisfactory and leads to purer products owing to its having no tendency to rearrange the resulting nitro-compound into an oxime (compare Barnett, Cook, and Grainger, J., 1922, **121**, 2065). The facile addition of nitro-groups appears to be common to all anthracene derivatives in which the "bridge" is intact, and in this way the "bridge" exhibits very close analogy to an ethylenic bond (compare Wieland, *Annalen*, 1922, **421**, 2065). The resulting compounds should, in the majority of cases, be capable of existing in *cis*- and *trans*-forms, and as evidence has recently been obtained (Barnett and Matthews, *Rec. trav. chim.*, 1924, **43**, 534; Barnett, Cook, and Matthews, *ibid.*, 1925, **44**, 217, 728, 818) that the geometrical configuration and the stability of compounds formed by addition to the "bridge" are profoundly influenced by the presence of other substituents in the molecule, the action of nitrogen dioxide on several anthracene derivatives has been examined, with the following results.

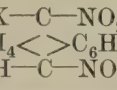
(i) Neither *meso*- nor *Bz*.-substituents have any appreciable influence on the ease with which addition to the "bridge" takes place, 9 : 10-dibromoanthracene, for example, reacting with nitrogen dioxide almost as easily as anthracene itself.

(ii) *Bz*.-Substituents do not increase the stability of the compounds formed by the addition of nitro-groups to the "bridge,"

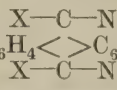
whereas in the case of the addition of halogen atoms, the presence of chlorine atoms in α-positions results in an enormous increase in stability (Barnett and co-workers, *loc. cit.*).

(iii) *Ms.*-Substituents appear to decrease the stability of the 9 : 10-dinitro-9 : 10-dihydroanthracenes.

(iv) Any compound of the general formula I will undergo re-establishment of the " bridge " with great ease on treatment with pyridine.



(I.)



(II.)

If X is a hydrogen atom, this re-establishment is brought about by loss of nitrous acid and formation of a derivative of 9-nitroanthracene. If X is a nitro-group, loss of nitrous acid and formation of a derivative of 9 : 10-dinitroanthracene take place. If X is a halogen atom, loss of halogen acid takes place. This last point is interesting, as Schaarschmidt (*Ber.*, 1924, **57**, 2065; 1925, **58**, 499) has shown that the action of nitrogen dioxide on halogen benzenes, with or without the addition of aluminium chloride, leads to the production of nitrohalogen benzenes, the *p*-isomeride predominating, often almost to the complete exclusion of the *o*-isomeride. In Schaarschmidt's experiments intermediate additive compounds were undoubtedly formed (and actually isolated in the impure state in combination with aluminium chloride). Since these lose nitrous acid rather than halogen acid, their structure must be different from that of those additive compounds formed by addition to an anthracene " bridge." This difference may be due to addition having taken place to a double bond (Kekulé formula). Alternatively, addition may have taken place to a " bridge " (Dewar formula), the different behaviour of the benzene and anthracene derivatives lying in their geometrical configuration, *cis-* in the case of anthracene derivatives, *trans-* in the case of benzene derivatives. Owing to the very unstable nature of the additive compounds it is extremely difficult to decide which of these alternatives is correct.

(v) Compounds of the general formula II, where X represents halogen, are extremely unstable and pass readily at the ordinary temperature into 9-nitro-9-halogen anthrone (when X is bromine) or into the corresponding anthraquinone (when X is chlorine).

(vi) When the molecule is unsymmetrical, loss of nitrous acid from a derivative formed by the addition of nitrogen dioxide may or may not lead to the same nitro-compound as is formed by loss of water from the compound (nitrodihydroanthranol) obtained by the addition of nitric acid to the " bridge."

Experimental.

Nitrogen dioxide generated by heating a mixture of lead nitrate and sand was passed into a solution or suspension of the anthracene derivative in chloroform, the whole being well cooled in a freezing mixture. The increase in weight gave the amount of nitrogen dioxide used; except where otherwise stated, it was found best to use excess. As a rule the reaction was complete in a few minutes, but in all cases the whole was kept in a freezing mixture for an hour before working up. The additive compounds were isolated by diluting and washing with light petroleum and recrystallising the solid, usually from luke-warm chloroform–light petroleum. Owing to the unstable nature of the additive compounds, recrystallisation is often very troublesome, and it was generally found best not to attempt to crystallise more than a gram at a time. The products can only be dried in a vacuum desiccator at the ordinary temperature, and they retain solvent very obstinately. They are all colourless, crystalline solids.

9-Nitroanthracene and 9 : 10-dinitroanthracene (m. p. 310°, not 294° as given in the literature) were prepared very easily by the action of cold pyridine and alcohol on the additive compounds obtained from anthracene and 9-nitroanthracene respectively.

1-Chloroanthracene gave an additive compound, which, owing to its slight power of crystallisation, could not be obtained pure. The crude substance on treatment with pyridine and alcohol in the cold gave 1-*chloro*-9 (*or* 10)-*nitroanthracene* (golden-yellow needles from alcohol or glacial acetic acid, m. p. 155°) which is different from the chloronitro-compound produced by the action of pyridine on the additive compound obtained from 1-chloroanthracene and nitric acid (Barnett and Matthews, *Rec. trav. chim.*, 1924, **43**, 538) (Found: N, 5·4. $C_{14}H_8O_2NCl$ requires N, 5·4%).

2-Chloroanthracene gave an additive compound which could only be obtained as a viscous oil. This with pyridine and alcohol gave a yellow solid which was obviously a mixture of isomeric chloronitro-compounds, but no simple method of separation was found.

1 : 5-*Dichloro*-9 : 10-*dinitro*-9 : 10-*dihydroanthracene* was obtained from 1 : 5-dichloroanthracene. It retains chloroform very obstinately; the sample analysed had been recrystallised, although with very heavy loss, from warm acetone (Found: N, 8·0. $C_{14}H_8O_4N_2Cl_2$ requires N, 8·3%). On heating, it turns yellow and then melts at 156° with violent evolution of gas. With cold pyridine and alcohol it passes very readily into 1 : 5-dichloro-9-nitroanthracene.

The additive compound from 1 : 8-dichloroanthracene could not

be obtained free from solvent, and a sample dried for 5 days in a vacuum desiccator gave a strong carbylamine reaction (Found: N, 5·7 after 1 day, 5·65 after 5 days. $C_{14}H_8O_4N_2Cl_2,1\frac{1}{2}CHCl_3$ requires N, 5·4%). It melts at 215° with violent evolution of gas, after turning yellow at a much lower temperature. On treatment with cold pyridine and alcohol it gave the same 1 : 8-dichloro-9 (or 10)-nitroanthracene as is obtained by the action of pyridine on the additive compound of nitric acid and 1 : 8-dichloroanthracene (Barnett and Matthews, *loc. cit.*).

9-*Bromo*-9 : 10-*dinitro*-9 : 10-*dihydroanthracene*.—The quantities used were 4 g. of nitrogen dioxide, 10 g. of 9-bromoanthracene, and 20 c.c. of chloroform. The solid collected after keeping for an hour and identified after recrystallisation as 9 : 10-dibromoanthracene was a by-product and was not present in the original 9-bromoanthracene. The main product, twice recrystallised, was colourless; on heating, it turned yellow and then sintered at about 115°, but had no definite melting point (Found: N, 8·0. $C_{14}H_9O_4N_2Br$ requires N, 8·0%). 9 : 10-Dinitroanthracene was the sole product obtained by the action of pyridine and alcohol.

9-*Bromo*-9-*nitroanthrone*.—The quantities were 5 g. of nitrogen dioxide, 10 g. of 9 : 10-dibromoanthracene, and 25 c.c. of chloroform; the period of keeping was about 2 hours. The product, recrystallised twice, formed colourless, silky needles which sintered at 116° and agreed in their general properties with the description of 9-bromo-9-nitroanthrone given by Meisenheimer (*Annalen*, 1904, **330**, 181) (Found: N, 4·45. Calc., N, 4·4%). This compound passes into anthraquinone very easily. The reaction is probably decomposition rather than hydrolysis, as it was completed in a few minutes when the compound was added to boiling benzene which had been dried for several weeks over metallic sodium.

9 : 10-*Dichloro*-9 : 10-*dinitro*-9 : 10-*dihydroanthracene*.—The solid obtained from 7 g. of nitrogen dioxide and 12·5 g. of 9 : 10-dichloroanthracene in 50 c.c. of chloroform was washed with cold chloroform–light petroleum and then twice recrystallised from chloroform. It is extremely unstable and decomposes almost at once into anthraquinone on boiling with chloroform, but by working with amounts of about 0·5 g., dissolving these in chloroform at 30°, and at once cooling the solution in a freezing mixture, snow-white crystals were obtained. Owing to the rapid decomposition which takes place at the ordinary temperature it was found necessary to analyse the product after drying it for an hour in a vacuum desiccator over concentrated sulphuric acid (Found: N, 8·0. $C_{14}H_8O_4N_2Cl_2$ requires N, 8·3%).

1 : 5 : 9-*Trichloro*-9 : 10-*dinitro*-9 : 10-*dihydroanthracene*.—The product from 3 g. of nitrogen dioxide and 7 g. of 1 : 5 : 9-trichloroanthracene in 15 c.c. of chloroform, after being twice crystallised, was a slightly yellow, crystalline powder which on heating decomposed with violent evolution of gas at 156° (Found in material dried for 3 hours : N, 7·4. $C_{14}H_9O_4N_2Cl_3$ requires N, 7·5%).

1 : 5-*Dichloro*-9 : 10-*dinitroanthracene* was obtained by the action of cold pyridine and alcohol on the above trichlorodinitrodihydroanthracene. After being twice recrystallised from pyridine, it formed pale yellow needles, m. p. 277° (Found : N, 8·3. $C_{14}H_6O_4N_2Cl_2$ requires N, 8·3%).

2 : 3 : 9-*Tribromo*-9-*nitroanthrone*.—Excess of nitrogen dioxide was passed into a well-cooled suspension of 10 g. of 2 : 3 : 9 : 10-tetrabromoanthracene in 50 c.c. of chloroform, and the whole kept for 3 hours in a freezing mixture. Unchanged tetrabromoanthracene was removed, the filtrate diluted with light petroleum, and the solid which separated washed with light petroleum and then twice recrystallised from warm chloroform–light petroleum (Found : N, 2·8. $C_{14}H_6O_3NBr_3$ requires N, 2·9%). When heated with toluene, this product evolves brown fumes and passes quantitatively into 2 : 3-dibromoanthraquinone.

The products obtained by the action of nitrogen dioxide on anthranyl methyl ether, 9-phenylanthracene or 9-phenylanthranyl methyl ether were, not additive compounds, but 9-nitroanthrone, 9-nitro-10-phenylanthracene and 9-phenyl-9-hydroxyanthrone respectively, all of which were identified by direct comparison with authentic samples.

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LONDON, E.C. 3. [*Received, July 6th*, 1925.]

CCLXXIX.—*The Constitution of Indian Kamala. Part I.*

By SIKHIBHUSHAN DUTT.

KAMALA was first investigated by Anderson, who isolated from it a crystalline compound, rottlerin, $C_{11}H_{10}O_3$ (*Edin. New Phil. J.*, 1855, **1**, 300). This has been investigated by various chemists including A. and W. Perkin (*Ber.*, 1886, **19**, 3109), A. G. Perkin (J., 1893, **63**, 975), Jawein (*Ber.*, 1887, **20**, 182), Telle (*Arch. Pharm.*, 1906, **244**, 441), Bartolotti (*Gazzetta*, 1894, **24**, ii, 480). A. G. Perkin (J., 1895, **67**, 230) obtained from it *o*- and *p*-nitrocinnamic acids, *p*-nitrobenzaldehyde, and *p*-nitrobenzoic acid by the action

of fuming nitric acid, and acetic and benzoic acids and phloroglucinol by fusion with potassium hydroxide. The present investigation was undertaken with a view to elucidate further the constitution of the substance.

Benzene is the most suitable solvent for extracting the colouring matter from kamala, as it dissolves very little of the resin. The pure colouring matter is best crystallised from toluene. The m. p. (206—207°) of the rottlerin isolated by the author is 15° higher than that recorded by A. G. Perkin (Telle, *loc. cit.*, gives m. p. 203—204°); the two substances, however, appear to be almost identical in chemical properties.

On treatment with acetic anhydride rottlerin yields a colourless, crystalline *hepta-acetyl* derivative melting at 165°; Perkin isolated a hexa-acetyl derivative as a yellow, crystalline powder melting at 130—135°. Possibly rottlerin contains, in addition to six phenolic hydroxyl groups, an alcoholic hydroxyl group which can be acetylated only under suitable conditions. In support of this view is the fact that only *hexamethoxy* and *hexabenzoyl* derivatives are obtainable from rottlerin by the action of methyl sulphate and benzoyl chloride in presence of dilute sodium hydroxide solution —conditions under which an alcoholic hydroxyl group is scarcely attacked at all.

Acetylrottlerin and acetylmethoxyrottlerin form dibromo-additive compounds. This indication of the presence of a double bond in rottlerin is supported by the fact that the action of fuming nitric acid on the substance produces a large quantity of *p*-nitrocinnamic acid.

On fusion with potassium hydroxide rottlerin yields phloroglucinol as the only phenolic compound, and on oxidation with permanganate acetyl- and methoxy-rottlerin are converted into triacetyl- and trimethyl-phloroglucinoldicarboxylic acids, respectively. These facts indicate that rottlerin contains two phloroglucinol residues joined to the parent structure by either one or two side chains; if by one side chain, an alkyl substituent is present in the phloroglucinol nucleus. Moreover, as phthalic and terephthalic acids are almost always formed in the oxidation of rottlerin, there appear to be two more benzene nuclei in its molecule, containing side chains in ortho-positions in the one and in para-positions in the other. The two acids, however, may be produced by selective elimination of a side chain from the same benzene nucleus containing three side chains in the 1 : 2 : 4-positions. This alternative is the more probable, for the presence of five benzene nuclei would account for thirty out of the thirty-three carbon atoms in the molecule of rottlerin; there would remain

only three carbon atoms, two of which must be present in the side chain containing the double bond. In all probability, therefore, rottlerin contains four benzene nuclei, of which (1) two must be phloroglucinol residues, (2) one must be in the residue $C_6H_5 \cdot CH{:}CH \cdot C$, and (3) one must be a benzene nucleus containing at least three side chains.

Rottlerin is converted into a ketone, rottlerone, by the action of 2% sodium carbonate solution (Perkin, *loc. cit.*), and therefore appears to contain a secondary alcoholic hydroxyl group.

As Telle (*loc. cit.*) seems to have isolated the mono-, di-, and trimethyl ethers of phloroglucinol from the products of interaction of barium hydroxide solution, and of sodium hydroxide and zinc dust, and rottlerin, the phenolic hydroxyl groups in this would appear to be more or less methylated. The present author, however, obtained a negative result in the estimation of methoxyl by Zeisel's method. The phenolic portion of the rottlerin molecule is completely destroyed by the action of oxidising agents, but phenolic derivatives are obtained in large yields by oxidation of acetyl- and methoxy-rottlerin, in which the phenolic hydroxyl groups are protected from the action of the oxidising agent.

From the ease with which cinnamic acid and dihydrocinnamic acid are produced from rottlerin by the action of oxidising and reducing agents respectively, it seems that the molecule contains a group $C_6H_5 \cdot CH{:}CH \cdot CO\cdot$ or $C_6H_5 \cdot CH{:}CH \cdot C(OH)<$. The presence of this would account for the formation of benzaldehyde, benzoic acid, and their derivatives by the action of various reagents..

Experimental.

Preparation of Rottlerin.—Commercial kamala (150 g.) was passed through a 100-mesh sieve and heated under reflux with 1200 c.c. of benzene for 8 hours. The solution was filtered at once and again after 12 hours and concentrated to about 200 c.c. The colouring matter, which separated slowly in large, brownish-yellow plates, was washed with alcohol and twice recrystallised ftom toluene; rottlerin was thus obtained in large, glistening, brownish-yellow plates, m. p. 206—207° (yield about 9 g.) (Found: C, 69·2; H, 5·5; *M*, ebullioscopic in toluene, 585, 615, 598, by silver salt, 675. Calc. for $C_{33}H_{30}O_9$, C, 69·4; H, 5·2%; *M*, 570).

The substance is sparingly soluble in the usual organic solvents. In doiling toluene and amyl alcohol it dissolves to the extent of about 12%, but separates almost completely on cooling. It is very soluble in basic solvents like pyridine, quinoline, or aniline and also in alkali hydroxides and carbonates.

Acetylrottlerin, $C_{33}H_{23}O_9(C_2H_3O)_7$, prepared by boiling pure

rottlerin with acetic anhydride (5 parts) and a few drops of pyridine and crystallised from dilute acetone, acetic acid, and alcohol, was obtained in colourless needles, m. p. 165° [Found: C, 64·9; H, 5·2. $C_{33}H_{23}O_9(C_2H_3O)_7$ requires C, 65·3; H, 5·0%]. An estimation of acetyl by Perkin's method confirmed the presence of 7 such groups.

Dibromoacetylrottlerin, $C_{33}H_{23}O_9Br_2(C_2H_3O)_7$.—Acetylrottlerin and bromine (in slight excess of 1 mol.) were allowed to react in cold glacial acetic acid. The mixture, which was not completely decolorised on gentle warming, was poured into water; the precipitate crystallised from carbon disulphide in pale yellow, microscopic needles, m. p. 145° [Found: Br, 15·2. $C_{33}H_{23}O_9Br_2(C_2H_3O)_7$ requires Br, 15·6%].

Benzoylrottlerin, $C_{33}H_{24}O_9(C_6H_5{\cdot}CO)_6$, obtained by the Schotten-Baumann method, was a light yellow powder which could not be crystallised from any solvent. It was moderately soluble in most of the organic solvents, insoluble in alkali hydroxides, and did not melt below 300° (Found: C, 75·8; H, 4·5. $C_{75}H_{54}O_{15}$ requires C, 75·3; H, 4·5%).

Methoxyrottlerin, $C_{33}H_{24}O_3(OMe)_6$.—Rottlerin dissolved in 5% aqueous sodium hydroxide was shaken with excess of methyl sulphate, more alkali and methyl sulphate were added, and the process was repeated four or five times, the solution being kept alkaline. The mixture was then warmed on the water-bath for 1 hour and the yellow solid was collected after cooling and dissolved in ether. The ethereal solution was exhaustively extracted with dilute sodium hydroxide solution, and the ether evaporated; the residue crystallised from dilute acetic acid in pale yellow, microscopic needles, m. p. 135—137° [Found: C, 71·1; H, 6·9; OMe, 28·8. $C_{33}H_{24}O_3(OMe)_6$ requires C, 71·5; H, 6·4; OMe, 28·4%].

Acetylmethoxyrottlerin, $C_{33}H_{23}O_3(OMe)_6{\cdot}C_2H_3O$.—A mixture of 2 g. of methoxyrottlerin, 10 c.c. of acetic anhydride, and 1 drop of pyridine was boiled for ½ hour and poured into water. The colourless product crystallised from acetic acid in fine clusters of needles, m. p. 215—217° [Found: C, 70·2; H, 6·6. $C_{33}H_{23}O_3(OMe)_6{\cdot}C_2H_3O$ requires C, 70·7; H, 6·3%].

Dibromoacetylmethoxyrottlerin, $C_{33}H_{23}O_3Br_2(OMe)_6{\cdot}C_2H_3O$.—The procedure was that for preparing dibromoacetylrottlerin. The pale yellow product, which could not be crystallised, decomposed on heating and was moderately soluble in most of the organic solvents [Found: Br, 18·2. $C_{33}H_{23}O_3Br_2(OMe)_6{\cdot}C_2H_3O$ requires Br, 18·6%].

Action of Oxidising Agents on Rottlerin and its Derivatives.—(1) *Fuming nitric acid.* Rottlerin (10 g.) was gradually added to 50 c.c. of nitric acid (*d* 1·5), the temperature being always kept

below 0°. The colouring matter dissolved very easily and torrents of red fumes were evolved. After 1 hour, the mixture, which had become almost solid owing to separation of *p*-nitrocinnamic acid, was diluted somewhat with ice-cold nitric acid (*d* 1·4) and filtered; the crystals melted at 285° after crystallisation from alcohol. A further quantity of *p*-nitrocinnamic acid was obtained on pouring the nitric acid mother-liquor into ice-water. The filtrate on extraction with ether yielded a gum from which succinic acid was isolated. Acetic acid was detected in the mother-liquor. No *o*-nitrocinnamic acid, *p*-nitrobenzoic acid, or *p*-nitrobenzaldehyde could be isolated (compare Perkin, *loc. cit.*). *p*-Nitrobenzaldehyde and *p*-nitrobenzoic acid were formed in fairly good quantity if the mixture was allowed to warm during the reaction, but even so, no *o*-substituted derivative could be isolated.

(2) *Dilute nitric acid* (*d* 1·2). Rottlerin (10 g.) was heated on the water-bath for 72 hours with 200 c.c. of dilute nitric acid with occasional shaking; the brownish-yellow colour of the rottlerin had then disappeared and the liquid was thick with white crystals. The mixture was filtered; acetic acid was detected in the filtrate. The crystals gave benzoic acid on distillation in steam; the non-volatile portion, on repeated extraction with boiling water, yielded almost colourless needles of *p*-nitrobenzoic acid, m. p. 237°. A small quantity of phthalic acid was obtained by evaporating the aqueous filtrate to dryness and crystallising the residue from boiling water.

The residue left after extraction with boiling water was insoluble in almost all solvents. Heated under diminished pressure, it sublimed in long needles of terephthalic acid (the methyl ester melted at 139°, alone or mixed with methyl terephthalate) (Found: C, 57·5; H, 3·9; Ag in silver salt, 57·2. Calc., C, 57·8; H, 3·6; Ag, 56·8%).

(3) *Alkaline potassium permanganate.* Rottlerin (5 g.) dissolved in 250 c.c. of 3% sodium hydroxide solution was treated with 1% potassium permanganate until this was no longer decolorised. The solution was filtered, concentrated to small volume, and acidified. The white precipitate was distilled in steam, small quantities of benzoic and acetic acids passing over. The non-volatile residue on extraction with hot water, yielded a small quantity of phthalic acid, while the aqueous mother-liquor, on extraction with ether yielded an unidentified dibasic acid, $C_{18}H_{20}O_4$, which crystallised from glacial acetic acid in glistening prisms, m. p. 192°. The aqueous mother-liquor after extraction with ether contained oxalic acid (isolated as calcium salt). The insoluble residue left after all these operations was terephthalic acid.

(4) *Alkaline hydrogen peroxide.* The same substances are obtained by the prolonged action of hydrogen peroxide on a cold alkaline solution of rottlerin as by the action of potassium permanganate; some benzaldehyde also is produced and the yield of the unknown acid is greater.

(5) *Alkaline potassium ferricyanide.* The reaction, which was very slow in the cold, was completed in several hours in the warm. On acidifying the alkaline solution, a tarry mass was obtained, which on distillation in steam yielded small quantities of benzaldehyde and benzoic acid. From the dark brown, brittle residue, which was very soluble in alkali or ether, nothing definite could be isolated. On oxidation with alkaline permanganate, it yielded a mixture of phthalic and terephthalic acids and also a small quantity of another acid, m. p. 216°. The last appears to be a tribasic acid from the analysis of its silver salt, but it was not obtained in sufficient quantity for further examination.

(6) *Potassium persulphate.* Rottlerin (5 g.) dissolved in 150 c.c. of concentrated ice-cold sulphuric acid was gradually treated with 14 g. of finely powdered potassium persulphate with stirring, until carbon dioxide was no longed evolved. The solution, which became colourless after being stirred for 2 hours, was poured on to ice, and the precipitate collected; acetic acid was detected in the filtrate. The precipitate was separated by steam distillation into volatile benzaldehyde and benzoic acid and non-volatile phthalic and terephthalic acids with only traces of cinnamic acid. The unknown dibasic acid, which is an almost constant oxidation product of rottlerin, was not formed.

(7) *Fusion with potassium hydroxide.* Ten grams of rottlerin were gradually added to 100 g. of potassium hydroxide and 10 c.c. of water at 100°; the mixture was then heated at 180—200° for ½ hour. The cold melt was dissolved in water, acidified with concentrated hydrochloric acid, extracted with ether, and the ether evaporated. The dark brown, viscous mass thus obtained, which had a strong odour of acetic acid, gave, on steam distillation, acetic and benzoic acids. An ethereal extract of the residue, on decoloration with animal charcoal and concentration at the ordinary temperature, yielded large, transparent leaflets of phloroglucinol, m. p. 218°. The ethereal mother-liquor on complete evaporation left a brown gum from which nothing definite could be isolated.

Action of Reducing Agents.—(1) *Zinc dust and sodium hydroxide.* A mixture of 5 g. of rottlerin, dissolved in 150 c.c. of 5% sodium hydroxide, and 20 g. of zinc dust was heated on the water-bath for 1 hour, and the colourless solution was filtered and acidified with hydrochloric acid. The yellowish-white, viscous mass obtained,

on distillation in steam, gave an acid distillate from which small quantities of succinic and acetic acids were isolated. The non-volatile residue, on cooling, solidified to a brown, brittle mass, from which dihydrocinnamic acid was isolated by extracting the powdered substance with sodium bicarbonate solution. The final dark brown residue could not be crystallised, nor could anything definite be isolated from it. It gave a dark violet coloration with ferric chloride, dissolved in sodium hydroxide or carbonate solution with a dark brown colour, and on fusion with potassium hydroxide at 200°, yielded comparatively large quantities of phloroglucinol.

(2) *Tin and hydrochloric acid.* A mixture of 10 g. of rottlerin with 20 g. of tin dust was heated with 150 c.c. of fuming hydrochloric acid on the water-bath with frequent stirring until all the tin had dissolved. The mass was diluted with water and filtered hot. The filtrate on extraction with ether yielded small quantities of acetic and succinic acids. The tarry residue on extraction with sodium bicarbonate yielded 1·3 g. of dihydrocinnamic acid. The residue, which could not be crystallised, yielded phloroglucinol on fusion with potassium hydroxide.

(3) *Sodium hyposulphite.* Rottlerin in alkaline solution, on treatment with sodium hyposulphite, yielded a brown, tarry mass from which only dihydrocinnamic acid could be isolated.

(4) *Hydriodic acid and red phosphorus.* A mixture of 5 g. of rottlerin, 2 g. of red phosphorus, and 20 c.c. of hydriodic acid (*d* 1·75), when heated in a sealed tube at 230—250° for 6 hours developed great pressure, due to what was probably a gaseous aliphatic hydrocarbon, and separated into two layers. The upper dark brown, oily layer, isolated by means of ether, distilled between 135° and 260°; decomposition then set in. The largest fraction b. p. 145—160°, on redistillation gave, between 152° and 159°, a colourless liquid with an odour resembling that of mesitylene. It was probably *n*-propylbenzene (Found: C, 89·7; H, 10·2. Calc. C, 90·0; H, 10·0%), but only a small quantity was available for examination. When heated with fuming nitric acid, it yielded a very small quantity of a crystalline acid, m. p. 140°, which did not depress the m. p. of *m*-nitrobenzoic acid.

(5) *Pyrogenic reduction with zinc dust.* Ten grams of rottlerin were distilled with zinc dust in the usual way in a stream of hydrogen. Gaseous hydrocarbons were evolved. The distillate which was collected in a receiver cooled in a freezing mixture consisted of a mixture of a crystalline solid and a liquid. The latter was absorbed in porous plate; the solid, crystallised from alcohol gave colourless plates, m. p. 190°, of β-methylanthracene and yielded β-methylanthraquinone on oxidation with nitric acid

The liquid, extracted from the porous plate with ether, was colourless, had b. p. 230—240°, and could not be identified; it was not obtained in sufficient quantity for analysis or quantitative examination.

Oxidation of Acetylrottlerin with Permanganate.—Acetylrottlerin (20 g.) suspended in 500 c.c. of water was oxidised at 80° with 25 g. of potassium permanganate in 5% solution, kept neutral by the addition of 10 g. of copper sulphate. The excess of permanganate was destroyed by ferrous sulphate, and the solution filtered. The filtrate, on evaporation to a small volume and acidification, yielded a small quantity of benzoic acid; the mother-liquor contained oxalic and acetic acids.

The precipitated oxides of manganese, iron and copper were suspended in water and dissolved by passing a current of sulphur dioxide. The brown, crystalline residue was extracted with boiling water, and from the solution a small quantity of phthalic acid was obtained. The insoluble residue, on extraction with alcohol, left terephthalic acid. The alcoholic extract, after decoloration with animal charcoal and dilution with hot water, yielded triacetylphloroglucinoldicarboxylic acid in glistening prisms, m. p. 260—270° (decomp. and evolution of carbon dioxide) (Found : C, 49·2; H, 3·7; Ag in the silver salt, 39·4. Calc. for $C_{14}H_{12}O_{10}$, C, 49·4; H, 3·5%. Calc. for $C_{14}H_{10}O_{10}Ag_2$, Ag, 38·9%). The ethyl ester, prepared in the usual way, melted at 96° and was identical with that described by Moore (J., 1904, **85**, 167). On deacetylation with concentrated sulphuric acid in absolute alcohol, the acid yielded ethyl phloroglucinoldicarboxylate, m. p. 106° (Moore, *loc. cit.*).

On heating in a vacuum at 220°, the acid evolved carbon dioxide. The melt was dissolved in ether, washed with very dilute sodium hydroxide, decolorised with animal charcoal, and the solution evaporated; colourless prisms, m. p. 105°, of triacetylphloroglucinol were thus obtained. When this was hydrolysed by solution in strong sulphuric acid, phloroglucinol was produced in quantitative yield.

Oxidation of Methoxyrottlerin with Permanganate.—Methoxyrottlerin was oxidised by a boiling neutral solution of potassium permanganate and the reaction products were isolated in the ways described above. Benzoic, acetic, phthalic, and terephthalic acids were obtained together with trimethylphloroglucinoldicarboxylic acid, which crystallised from dilute alcohol in glistening, white needles, m. p. 248—255° (decomp. and evolution of carbon dioxide) (Found : C, 51·3; H, 4·8; Ag in the silver salt, 46·4. Calc. for $C_{11}H_{12}O_7$, C, 51·5; H, 4·6%. Calc. for $C_{11}H_{10}O_7Ag_2$, Ag, 45·95%). The acid was heated at 240° for ½ hour until the evolution of carbon

dioxide had ceased, and then distilled. A colourless liquid passed over at 250—255° and solidified in the receiver to a crystalline mass of glistening leaflets, m. p. 50—51°, of trimethylphloroglucinol. This gave a quantitative yield of phloroglucinol on hydrolysis with concentrated hydriodic acid.

The greater part of this work was done in the Laboratories of the Dacca College and the Dacca University during 1921–1923. My best thanks are due to Mr. Nirmal Kumar Sen for his help in the preparation of large quantities of rottlerin, and to Dr. E. R. Watson and Dr. P. C. Ghosh for their kind encouragement during the progress of the work.

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CCLXXX.—*The Decomposition of Carbon Monoxide in the Corona due to Alternating Electric Fields. Part I.*

By MIGUEL CRESPI and ROBERT WINSTANLEY LUNT.

IN the course of experiments repeating the work of Moser and Isgarischeff (*Z. Elektrochem.*, 1910, **16**, 613) on the decomposition of carbon dioxide when submitted to the corona produced by alternating electric fields of commercial frequencies, one of the authors (R. W. L.) observed the formation of a solid substance the properties of which appeared to be similar to those of the solid obtained by Brodie when investigating the action of the electric discharge on carbon monoxide (*Annalen*, 1873, **169**, 270; *Proc. Roy. Soc.*, 1873, **21**, 245). The chief characteristics assigned to the solid by Brodie were a dark brown colour, high solubility in water and alcohol (the former solution giving a marked acid reaction), and a very low solubility in ether. Basing his arguments on the composition of the gas phase before and after exposure to the discharge, Brodie stated that there appeared to be two oxides, possibly two of a series, to which he assigned the formulæ C_4O_3 and C_5O_4. Four years later, Berthelot (*Ann. Chem. Phys.*, 1877, **10**, 72) repeated some of Brodie's work and assigned the formula C_4O_3 to the solid substance he prepared.

In view of the scanty information existing on this interesting compound of carbon and oxygen experiments have been carried out with the aim of describing in some detail the properties of this material and the conditions under which it is produced. The difficulties encountered in producing appreciable quantities of the

solid substance have occasioned some delay in completing a survey of its properties and this communication will therefore be confined to an account of the behaviour of carbon monoxide when subjected to alternating electric fields of frequency 250 over the pressure range 760 to 80 mm. Hg.

Experimental.

Description of Apparatus.—Source and Measurement of Electric Power. Single-phase alternating current of frequency 250 was supplied from a motor alternator set and transformed up to the required voltage over the range 2000 to 10,000 volts. The voltage applied to the reaction vessel was measured by a Kelvin-White instrument and the current flowing through it was indicated approximately by a dynamometer type milliameter reading 0—50 milliamperes.

Reaction Vessel. A glass vessel fashioned in the usual manner of a Siemen's ozoniser, that is to say, constructed of concentric cylinders, served to contain the gas during exposure to the discharge. One end of the inner tube was closed and the other was ground to fit into the outer tube; it could therefore be removed from the outer tube when necessary. Surrounding the outer tube was a glass jacketing tube which was filled with mercury and served as the high-tension electrode. The inner tube was filled with mercury and constituted the other electrode, which was earthed. It was cooled by a stream of water at room temperature flowing through a thin-walled glass tube immersed in the mercury. The temperatures of each electrode were recorded by alcohol thermometers, it having been observed that mercury thermometers rapidly fouled under the experimental conditions obtaining.

The reaction vessel was so arranged that carbon monoxide could be fed in from a reservoir or the vessel connected to a Töpler pump; it was also connected to a mercury manometer. The volume of gas in the connecting capillary tubes which was out of contact with the discharge was reduced to a minimum. The diameters of the outer wall of the vessel were 22·4 mm. (external) and 21 mm. (internal), and of the inner wall 16 mm. (external) and 14·8 mm. (internal). The length of electrodes was approx. 300 mm.

Preparation of Carbon Monoxide.—The gas produced by dropping recrystallised formic acid into an evacuated flask containing warm sulphuric acid was passed over solid potash and dried by flowing through some 6 feet of tubing packed with phosphorus pentoxide. It was analysed by exposure to alkaline pyrogallol and by absorption in ammoniacal cuprous chloride solution, in which the gas was completely soluble. The gas so prepared was free from oxygen.

Measurements and Results.—Two sets of observations were carried out, one at 4500 volts and the other at 9000 volts. In every case the heat generated in the reaction vessel was sufficient to raise the mean temperature of the vessel several degrees above the room temperature despite the cooling of the inner electrode.

In order to follow the pressure change during exposure to the discharge it became necessary to know the value of the mean temperature of the vessel, T_m, corresponding to any two given values of the temperature of the outer and inner electrodes, T and T_1, respectively. The following empirical relationship was observed to hold

$$\log T_m = k \log T_1 + (1 - k) \log T$$

with an accuracy of about 1%. The value of k was determined in several cases by observing the pressure of the gas, p_1, corresponding to electrode temperatures, T and T_1, and the pressure, p_2, of the same gas when the whole system was allowed to reach a uniform temperature, T_2. We then have

$$(T_m + 273)/(T_2 + 273) = p_1/p_2.$$

Substituting the values so obtained for T_m in the above equation, the mean value of k was found to be 0·737.

Preliminary experiments established that the sole products of the reaction were the brown solid, which is deposited on the walls of the reaction vessel, and a residual gas mixture of carbon monoxide and dioxide, containing not more than traces of oxygen.

The experimental procedure was to introduce carbon monoxide into the evacuated reaction vessel and to record the pressure of the gas in the reaction vessel and the temperature of the two electrodes every quarter of an hour from the commencement of the discharge until sensible equilibrium was reached, as indicated by the cessation of pressure change.

After discontinuing the discharge, the residual gas was pumped off and analysed by absorbing the carbon dioxide present with solid potash. Knowing the composition of this residual gas and the values of the gas pressure before and after exposure to the discharge, the composition of the solid substance produced can readily be calculated.

The brown solid deposited on the walls of the vessel has no appreciable vapour pressure.

The results are given in Tables I and II: p_0 and p_∞ are the initial and the equilibrium pressure (mm. of Hg at 0°) of the gas in the reaction vessel; t is the time (mins.) required to reach sensible equilibrium; a is the ratio C/O in the solid; and b is the ratio CO/CO_2 in the equilibrium gas mixture.

TABLE I.

Voltage applied to reaction vessel = 4500 volts r.m.s.
Current flowing through reaction vessel = 1·0 milliamperes (approx.).

p_0.	p_∞.	a.	b.	t.	$(p_0 - p_\infty)/t$.
501·7	344·0	1·204	11·89	225	0·70
317·6	219·1	1·228	11·00	150	0·66
201·4	145·4	1·256	11·76	75	0·74
141·6	110·1	1·335	12·93	60	0·86
105·3	83·2	1·348	13·59	35	0·63
78·7	61·5	1·409	11·22	25	0·69
			mean 12·07		mean 0·71

TABLE II.

Voltage applied to reaction vessel = 9000 volts r.m.s.
Current flowing through reaction vessel = 2·5 milliamperes (approx.).

p_0.	p_∞.	a.	b.	t.	$(p_0 - p_\infty)/t$.
501·0	327·5	1·186	11·27	225	0·77
304·7	213·4	1·267	10·11	135	0·68
193·3	140·8	1·274	11·04	90	0·61
130·8	100·2	1·308	12·63	35	0·87
94·4	73·7	1·398	11·49	25	0·82
			mean 11·82		mean 0·77

The curves representing the velocity of reaction can be derived from the following expression :—

$$-dp_t/dt = (k + tk')(p_t - p_\infty),$$

where p_t denotes the pressure at any time t, and k and k' are constants which appear to be functions of the initial pressure and of the electrical conditions, although the time required to reach sensible equilibrium seems to be practically independent of the latter. The form of these functions remains to be determined. The observed values of p_t and those calculated from the above equation are set forth in Tables III and IV; the agreement obtaining is satisfactory and not uninteresting. The values of the mean rate of decrease of pressure, which are cited in the sixth column of Tables I and II show a remarkable constancy.

The wide range of electrical and pressure conditions obtaining being borne in mind, one of the most interesting results is the constancy observed in the composition of the residual gas when equilibrium is reached. This approximates closely to a mixture of one volume of carbon dioxide with twelve volumes of carbon monoxide.

The composition of the solid substance appears to be independent of the electrical conditions over the range examined, and solely dependent on the gas pressure, the ratio of carbon to oxygen in the solid substance increasing continuously with decreasing gas pressure.

Table III.

Voltage applied to reaction vessel = 4,500 volts r.m.s.
Pressures as before in mm. Hg. (0°).

	k = 0·0127. k' = 0·00023.		k = 0·0102. k' = 0·00062.		k = 0·0828. k' = 0·00388.		k = 0·0801. k' = 0·00679.	
Time in mins.	p obs.	p calc.	p obs.	p calc.	p obs.	p calc.	p obs.	p calc.
0	501·7	501·7	317·6	317·6	141·6	141·6	105·3	105·3
5	—	—	—	—	—	—	98·0	98·0
10	—	—	—	—	—	—	91·5	91·5
15	474·9	474·4	296·6	294·0	119·2	119·2	87·2	87·1
30	447·5	446·4	272·0	274·0	111·2	111·2	—	—
35	—	—	—	—	—	—	83·2	83·2
45	419·1	420·5	251·5	252·3	—	—		
60	398·0	398·2	238·4	236·6	110·1	110·1		
75	381·0	380·5	229·0	227·1	—	—		
90	367·5	367·4	223·2	222·2	—	—		
105	358·5	358·5	—	—	—	—		
120	—	—	—	—	112·4	110·1		
150	—	—	219·1	219·1	—	—		
195	344·2	344·2	—	—	—	—		
225	344·0	344·0	—	—	—	—		

Table IV.

Voltage applied to reaction vessel = 9,000 volts r.m.s.
Pressures as before in mm. Hg. (0°).

	k =0·00581. k'=0·00018.		k = 0·043. k'= 0.		k =0·0547. k'=0.		k =0·0700. k'=0.		k =0·232. k'=0.	
Time in mins.	p obs.	p calc.	p obs.	p calc.	p obs.	p calc.	p obs.	p calc.	p obs.	p calc
0	763·3	763·3	501·0	501·0	304·7	304·7	130·8	130·8	94·4	94·4
5	—	—	—	—	—	—	109·4	110·9	80·7	80·2
10	—	—	—	—	—	—	103·2	103·9	75·8	75·7
15	—	—	434·8	432·9	247·4	253·6	101·6	101·5	74·4	74·3
20	—	—	—	—	—	—	—	100·7	73·9	73·9
25	—	—	—	—	—	—	100·8	100·4	73·7	73·7
30	728·8	727·8	385·5	391·6	227·9	231·1	—	100·3	—	—
35	—	—	—	—	—	—	100·2	100·2	—	—
45	—	—	361·4	366·5	224·5	211·1	—	—		
60	675·4	674·5	350·8	351·2	220·8	216·8	—	—		
75	—	—	—	—	218·5	214·9	—	—		
90	621·9	622·2	—	—	—	—	102·8	100·2		
120	582·7	583·1	333·6	330·7	213·9	213·5	—	—		
135	—	—	—	—	213·4	213·4	—	—		
225	—	—	327·5	327·6	—	—	—	—		
300	541·5	541·5	—	—	—	—	—	—		

This observation is in agreement with the work of the Genera Electric Company's Research Staff on the disappearance of carbo monoxide in discharge tubes when operated at pressures less tha 1 mm. of mercury (*Phil. Mag.*, 1920, **40**, 585). They were of th opinion that at such pressures the monoxide decomposed to carbo and the dioxide, although no chemical tests were made to establis the formation of carbon.

In addition to possessing the properties recorded by Brodie and Berthelot the solid substance is very hygroscopic. In view of the small quantities of material available up to the present time the systematic examination of its chemical properties is reserved for a later communication.

Summary.

(1) A description has been given of the behaviour of carbon monoxide in the corona due to alternating electric fields of frequency 250. It decomposes giving a solid substance, containing carbon and oxygen, and a mixture of carbon dioxide and monoxide of approximately constant composition.

(2) The composition of the solid substance appears to be independent of the electrical conditions and varies solely with the gas pressure.

(3) In so far as the properties of the solid substance have been examined they are similar to those recorded by earlier investigators. In addition the substance has been found to be highly hygroscopic.

(4) Experiments are in progress to determine more completely the nature of the solid substance.

The authors wish to tender their thanks to the Ramsay Memorial Fellowship Trust for a Fellowship (M. C.) and to the Commissioners for the Exhibition of 1851 for a Senior Studentship (R. W. L.) which have enabled them to carry out this research, and particularly to Professor F. G. Donnan, F.R.S., for his deep interest and advice during the progress of the research.

The William Ramsay Inorganic and Physical Chemistry Laboratories,
University College, London. [*Received, May 27th,* 1925.]

CCLXXXI.—*Anode Phenomena in the Electrolysis of Potassium Ethyl Malonate.*

By John Braithwaite Robertson.

R. E. Gibson (this vol., p. 475) has shown that the synthesis of trichloromethyl trichloroacetate by electrolysis of trichloroacetic acid takes place only when the anode potential exceeds 2·34—2·37 volts on the hydrogen standard and concluded that the anode process is one of direct oxidation. However, as he points out, this is not a carbon to carbon synthesis, and it appeared desirable to determine whether similar results would be obtained in a true Kolbe synthesis.

As in the apparatus devised for measuring anode potentials, only small currents could be employed, and therefore only small quantities of synthetic product obtained, potassium ethyl malonate proved to be a very suitable material because, whereas this salt is very soluble in water, the diethyl succinate formed on synthesis is an oil and sparingly soluble in the solution employed. On production of this oil a change in the appearance of the gas bubbles leaving the anode was easily observable, as Gibson found to be the case with trichloroacetate. When no synthesis occurred, these were small in size and left the anode freely, but as soon as the oil was formed they became much larger and appeared to cling to the anode, a phenomenon attributable to their being coated with a thin film of the synthetic oil.

Preliminary experiments showed that a change occurred at a potential of about $\epsilon_H = 2{\cdot}3$, where ϵ_H is potential referred to the normal hydrogen electrode as standard. Below this potential the gas evolved at the anode was chiefly oxygen, whereas above this potential scarcely any oxygen was produced, the gas being almost pure carbon dioxide.

A series of determinations was carried out to fix this point more exactly. Measurements were made at different values of the applied *E.M.F.* between the electrodes of (1) the anode potential, (2) the current, and (3) the volume and composition of the gases evolved in unit time. Similar measurements were also made when electrodes of (1) platinised platinum, (2) grey platinum, and (3) gold were used. The apparatus employed is practically identical with that described by Gibson, except that here it was not necessary to have the anode and the cathode in separate compartments.

The potential difference between the anode and a calomel electrode was measured by the compensation method, with use of an Ostwald decade rheostat, a battery of accumulators, a sensitive galvanometer, and a standard cadmium cell. The current passing through the electrolyte was measured on a milliamperemeter, and the *E.M.F.* between the electrodes on a shunted voltmeter.

After all necessary connexions had been made, the current was switched on and the voltage adjusted to give the desired *E.M.F.* between the electrodes. Readings of the anode potential were made at intervals. The potential took a considerable time to become constant, in general about an hour, but in some cases several hours; with gold electrodes within a certain range no steady reading was obtained even after a constant *E.M.F.* had been applied for 12 hours. When equilibrium was reached, the evolved gases were collected for a measured length of time varying from $\frac{1}{2}$ hour to 3 hours (depending on the current passing) until

at least 20 c.c. were obtained. During this time frequent regular readings of anode potential and current were made, and the means of these were taken as representing the potential and current during the period. If these readings varied by more than a few hundredths of a volt or a few milliamperes, as the case might be, the experiment was abandoned. The amount of hydrogen found on analysis served as a check on the amperemeter readings. It was necessary to determine only the carbon dioxide and oxygen in the gas sample, the residue being hydrogen. Several tests with fuming sulphuric acid showed that no unsaturated hydrocarbon gases were produced.

The results are detailed on p. 2060 : c is the current in milliamperes, ϵ_H the anode potential, and CO_2 and O_2 are the volumes (c.c at *N.T.P.*) evolved per hour.

The solution used in each case was N-potassium ethyl malonate. The values for carbon dioxide do not represent the total carbon dioxide produced, as a considerable proportion of this remains in the solution, being fixed as carbonate or bicarbonate by the alkali formed round the cathode, but they are useful for purposes of comparison.

The diagrams show curves for oxygen evolved per hour and current carried plotted from the above data, the numbers of the diagrams corresponding with those of the tables on p. 2060.

With smooth platinum electrodes (Ib) there is, between anode potentials of 2·30 and 2·37, a sudden drop in oxygen evolved. A similar drop, although not so sharp, occurs with grey platinum electrodes (Ig) at a potential of about 2·4. The characteristic change in the nature of the bubbles leaving the anodes was also apparent about these points. This value of 2·3—2·4 therefore corresponds to the potential at which the synthesis of diethyl succinate occurs. A large-scale experiment with grey platinum electrodes and a current of 1 ampere showed that above this potential synthesis took place as with smooth platinum, a film of oil appearing on the surface of the electrolyte after about 15 minutes. This value of the anode potential is the same as that found by Gibson (*loc. cit.*) in the formation of trichloromethyl trichloroacetate. The shape of the current curve, however, differs from his. Whereas he found a drop in the curves on formation of the ester, here a fairly sharp rise takes place. In order to determine whether the difference was due to the different natures of the reactions or simply to differences in apparatus and working conditions, Gibson's experiment was repeated using the apparatus already described but replacing the platinum foil anode by one of platinum wire. With N-trichloroacetic acid, a similar curve to Gibson's was obtained.

Ib.

Electrodes : Two pieces of bright platinum foil, each 20 × 25 mm., 1 cm. apart.

$c.$	ϵ_H.	CO_2.	O_2.
20	2·02	0·7	2·3
24	2·12	0·7	3·0
31	2·16	1·5	4·1
37	2·27	1·7	5·3
44	2·30	2·1	6·2
63	2·37	4·0	2·6
88	2·39	7·0	2·5
123	2·45	20·6	0·5

Ig.

Electrodes : Grey platinum. Two pieces of foil, 10 × 10 mm., which had been platinised, then gently ignited in a spirit lamp flame, 1·5 cm. apart.

$c.$	ϵ_H.	CO_2.	O_2.
36	2·28	0·4	6·1
42	2·31	0·6	6·6
54	2·35	1·5	7·8
73	2·40	2·3	8·2
84	2·44	3·5	7·3
105	2·49	4·4	7·6
181	2·6—2·7	9·2	5·8

II.

Electrodes : Platinised platinum wire, 2 cm. long and 0·5 mm. in diameter, 1·5 cm. apart.

$c.$	ϵ_H.	CO_2.	O_2.
24	2·24	0·1	5·0
31	2·29	0·1	6·0
38	2·32	0·1	7·5
53	2·43	0·1	10·1
65	2·53	0·3	12·9
91	2·68	0·4	17·1
103	2·77	0·7	19·3
121	2·88	1·1	22·3
135	3·00	1·5	24·7
142	3·10	1·9	25·6
168	3·25	3·7	29·2
185	3·33	7·0	29·1
202	3·50	19·7	21·9
210	3·78	18·4	14·5

III.

Electrodes : Gold wires, 1 mm. in diameter, 1 cm. apart. In the first six experiments these were 2·5 cm. long. The length was then reduced to 0·5 cm. With a similar anode potential the current carried was then exactly 1/6th of that given with the larger electrodes. The actual results obtained for current and gases evolved in the first six experiments have been divided by 6 to make the whole series comparable.*

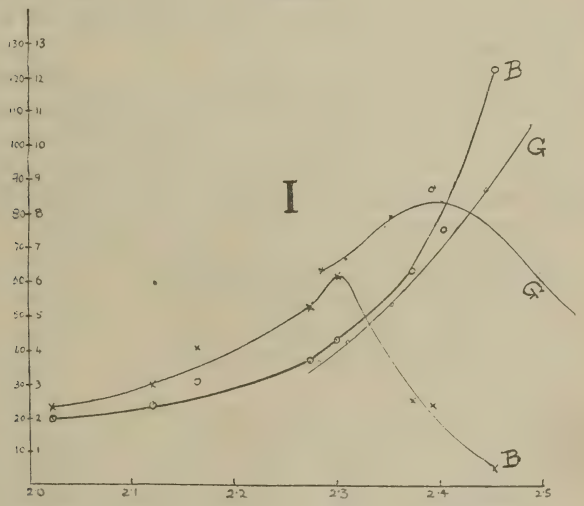
$c.$	ϵ_H.	CO_2.	O_2.
4·3	2·28	0·05	0·8
7·0	2·52	0·07	1·4
10·5	2·77	0·1	2·0
14·0	2·88	0·1	2·7
20	3·12	0·2	3·7
24	3·28	0·2	4·7
30	3·57	0·2	6·1
32	4·24	0·2	6·2
32	4·43	0·3	6·5
35	5·01	0·3	6·8
111	6·22	1·0	21·4
133	6·31	1·3	24·9
158	6·52	1·8	30·9
240	6·76	2·2	44·9

* The gold electrodes even under low potentials soon became coated with a brown covering of dispersed gold. The current and potential readings, however, were quite as constant as in the case of platinum, so it may be assumed that in spite of this "spattering" the surface area remained practically constant throughout.

This type of curve was also given when potassium trichloroacetate was used as electrolyte. With potassium ethyl malonate, however, a curve similar in all respects to that of Fig. 1 was obtained. The difference is therefore connected with the nature of the reactions at the anode and may be conditioned by the presence or

absence of halogen. Gibson assumes that the anode changes from "platinum α," which is stable at low potentials and which does not favour synthesis, to "platinum β," stable above 2·2 volts and favouring synthesis. The following facts would seem to lend support to this view. After a solution of potassium ethyl malonate had been electrolysed for a time at an anode potential above the synthetic value the applied *E.M.F.* was reduced so as to bring the anode potential below this value; the resulting current always approximated after a short interval to that obtained when ascending the curve. This was not the case when potassium trichloro-

FIG. 1.



Curve IB: *Bright platinum.* *Curve* IG: *Grey platinum.*

Horizontal axis: anode potential, ϵ_H, *in volts.*

Vertical axis: on left, current in milliamperes ⊙; *on right, oxygen per hour in c.c.* ×.

acetate was the electrolyte. For instance, a solution of the latter was electrolysed for 20 hours at a high potential. The anode potential was then 2·8 volts and the current 0·3 m.a. The applied *E.M.F.* was then reduced, the anode potential becoming 2·2 volts and the current 0·07 m.a. On the ascending curves the current corresponding to this potential was 0·65 m.a., nearly ten times as large. The anode was still covered with the large bubbles typical of synthesis, although the potential was now well below the synthetic potential. On removing these bubbles by rubbing with a piece of wire (without interruption of the current), although there was a momentary rise of current, it subsequently returned

rapidly to 0·07 m.a. as large bubbles reformed on the anode. Repeated rubbings effected no permanent change. The electrolysis was then allowed to proceed undisturbed for 5 days with the same constant applied *E.M.F.* At the end of this time, anode potential was still 2·2 volts, but the current had increased to 0·7 m.a., a value agreeing well with the 0·65 m.a. obtained in the ascending series. On Gibson's hypothesis, these results are simply explained by assuming that " platinum β " was formed on the surface of the anode during its period of high potential, that this " platinum β " continued to function as a synthetic agent on reduction of the potential below the normal synthetic value, but after the lapse of sufficient time it, being metastable at low potentials, had gradually reverted to " platinum α " with resulting cessation of synthesis and rise of current.

Interpretation of the Results.—When potassium ethyl malonate is electrolysed, the anion $CO_2Et{\cdot}CH_2{\cdot}CO{\cdot}O'$ is discharged at the anode. On discharge, this may react with the water, or with another similar anion, or the oxygen liberated from the water may oxidise ethyl hydrogen malonate. These possibilities are shown in the equations, where R stands for $CH_2{\cdot}CO_2Et$.

$$\text{Ia. } 2R{\cdot}CO{\cdot}O + H_2O = 2R{\cdot}CO_2H + O.$$
$$\text{Ib. } 2R{\cdot}CO_2H + O = R{\cdot}R + 2CO_2 + H_2O.$$
$$\text{II. } 2R{\cdot}CO{\cdot}O = R{\cdot}R + 2CO_2.$$
$$\text{III. } R{\cdot}CO_2H + 10\ O = 5CO_2 + 4H_2O.$$

Other subsidiary reactions may occur, but in the case of the malonates these are very limited in degree. Equation Ia represents the reaction of the anion with water with liberation of atomic oxygen. If this atomic oxygen unites with another atom, molecular oxygen is produced and escapes as gas at the anode. An equivalent quantity of hydrogen will be produced at the cathode by the reaction of the potassium ions, and the whole therefore amounts to the simple electrolysis of water. Equation Ib represents the formation of diethyl succinate as a result of the oxidation of the ethyl hydrogen malonate formed at the anode by the atomic oxygen simultaneously liberated. Equation II represents two discharged anions as uniting to form the same product, a molecule of carbon dioxide splitting off from each of them. Equation III represents complete oxidation of hydrogen ethyl malonate to carbon dioxide and water. It remains to determine which reactions prevail with the different electrodes and with different potentials. In general, equation Ia represents the prevailing reaction at low potentials. It would appear justifiable to look on this reaction as being maintained during rise of potential and to consider reaction Ib, II,

or III as being superimposed on it (compare Gibson, *loc. cit.*, p. 482).

FIG. 2.

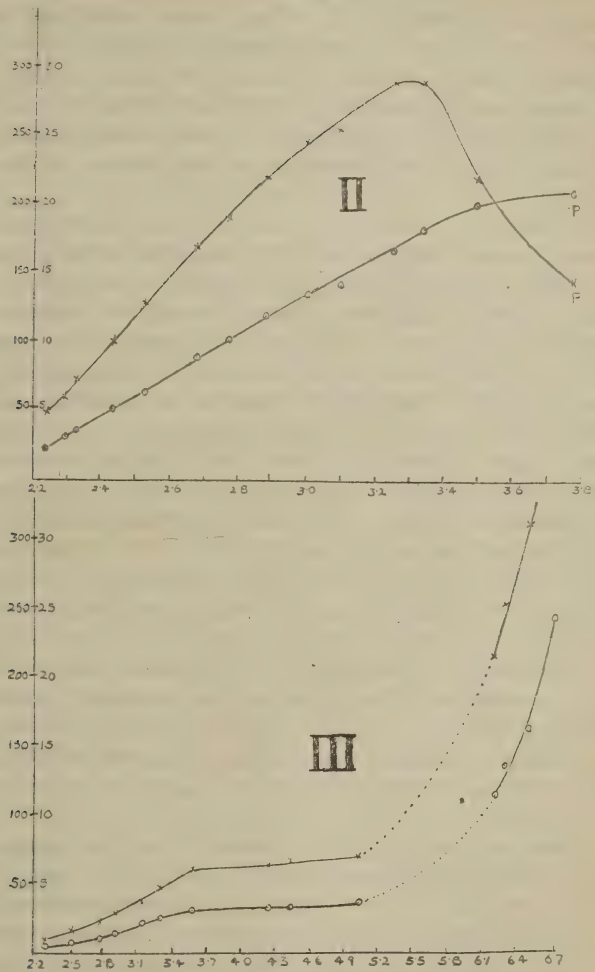


FIG. 3.

Curve II: *Platinised platinum.* *Curve* III: *Gold.*

Horizontal axis: anode potential, ϵ_H, *in volts.*
Vertical axis: on left, current in milliamperes ⊙; *on right, oxygen per hour in c.c.* ×.

There are then three possible forms of oxygen curve. (1) If reaction Ia alone holds throughout the whole range, the amount of oxygen evolved per unit time would be directly proportional to

the current, and would rise steadily with increasing potential, giving a continuously ascending curve. (2) If reaction II were superimposed at any stage, since no oxygen is either used up or produced by it, presumably the oxygen curve would here reach a maximum and then remain approximately at that value. (3) If either reaction Ib or III was superimposed, some of the oxygen formed in reaction Ia would be used for oxidation work and a fall in the value of oxygen evolved per unit time would thereby result.

We will now apply this reasoning in turn to each of the cases studied.

Bright Platinum (Curve Ib).—The oxygen curve rises with increase of potential and current to a maximum at a potential of 2·3 and then rapidly falls until at potential = 2·45 practically no oxygen is evolved. Synthesis of diethyl succinate therefore takes place at anode potential = 2·3, and this synthesis is performed with the help of the atomic oxygen liberated at the anode or according to equation Ib. This point is therefore an oxidation potential, not a discharging or decomposition potential, as it would be if equation II held. It will be noted also that the current curve begins to rise steeply about this point, although no break has been shown in the curve. This can be readily explained as being due to depolarisation of the anode resulting from the oxygen removal. At low potentials, the oxygen is never equal to half the hydrogen, as it would be if reaction Ia occurred alone, an appreciable quantity of carbon dioxide being always produced. This may result from either reaction Ib or III taking place, *i.e.*, either synthesis occurring below the apparently limiting potential or complete oxidation of part of the electrolyte. It is probable, as will be shown later, that the oxygen deficiency represents a complete oxidation of a small portion of the electrolyte to carbon dioxide and water (compare Murray, *loc. cit.*).

Grey Platinum (Curve Ig).—The curves for grey platinum resemble those for smooth platinum, the maximum in the oxygen curve being, however, less sharp. It is also noteworthy that before this point is reached the carbon dioxide evolved became relatively high as with smooth platinum. The reactions taking place are therefore probably the same in both cases. Although there is no direct experimental evidence to support the hypothesis, it seems probable that the comparative differences may be due to differences in surface current density.

Platinised Platinum (Curve II).—The oxygen and current curves rise steadily until an anode potential of about 3·3 is reached. The oxygen curve then falls while the current curve still ascends, although somewhat less steeply. If any synthesis takes place,

it is exceedingly small in amount, as is proved by the fact that on electrolysing 100 c.c. of solution between platinised platinum electrodes for 2 hours with a current of 2·5 amperes and extracting the resulting solution with ether, there remained on removal of the ether only a trace of an oily film which had not the characteristic odour of diethyl succinate. It would appear, therefore, that above an anode potential of 3·3 complete oxidation of the electrolyte (equation III) takes place in amount sufficient to produce a fall in the oxygen evolved. This is also shown by the larger increase in carbon dioxide. Below this value, only small quantities of carbon dioxide are produced, and relatively these are very much smaller compared with the oxygen evolved than is the case with smooth platinum. In order to test conclusively whether carbon dioxide is evolved at very low potentials, the following experiment was carried out. A modified apparatus was used which allowed a current of air free from carbon dioxide to be passed through the electrolyte. This was fitted with platinised electrodes and half filled with malonate solution to which a few drops of dilute sulphuric acid had been added. With no current passing, a slow stream of air was aspirated through the solution and then bubbled through a single drop of lime water contained in a small bubbling apparatus. After 2 hours there was no sign of milkiness in the lime water. This proved the malonate solution to be free from carbonate. A current of 10 milliamperes was then passed with an anode potential of 1·83, the same air current being continued. After $\frac{1}{4}$ hour there was evidence of carbon dioxide and after 1 hour the milkiness was very definite. Oxidation was therefore taking place even at this very low potential. Since there is little doubt that the only oxidation occurring with platinised platinum is the complete oxidation of equation III, this would support the conclusion that in the case of smooth platinum the carbon dioxide produced at low potentials is due to this reaction.

Gold (Curve III).—With gold electrodes at low potentials there is a very small yield of carbon dioxide, but its presence was proved by an experiment similar to that described in the case of platinised platinum. It probably represents a small amount of complete oxidation. The oxygen evolved rises steadily till a potential of 3·6 is reached, then remains practically constant till potential = 5·0. Thereafter occurs a region of oscillating potentials. With an applied *E.M.F.* between the electrodes of 7·3 volts, the current varied during 12 hours between the limits of 40 and 8 milliamps., with corresponding anode potential variation of 5·0—6·0. Both rise and fall were very slow, each occupying from 1 to 2 hours, and they showed no diminution in magnitude with time. Above

potential = 6·2, rapidly ascending smooth curves are obtained. The carbon dioxide evolved remains very small throughout and even at the highest potential reached the oxygen deficiency is only about 10%. It would thus appear that with gold there is very little oxidation of any kind, the main reaction throughout being that of equation Ia. The peculiar nature of the curves between anode potentials of 3·6 and 6·2 is doubtless due to some form of electrode effect, most probably the formation of an oxide of gold. On this assumption one can imagine that at potential 3·6 the atomic oxygen liberated at the anode, instead of combining to form molecular oxygen, begins to combine with the gold. This tendency continues until potential = 5·0, the gradual reduction in conductivity of the electrode due to the formation of the film of oxide rendering this portion of the curve flat. Above this potential, *i.e.*, throughout the dotted portion of the curve where readings were not obtainable, the oxide film is alternately formed and destroyed as the potential varies between about 5·0 and 6·0, the lower potential favouring the formation of oxide and the higher one causing it to decompose with oxidation of the electrolyte. The variation in the conductivity of the electrode during these changes accounts for the changes in current, which throughout shows oscillations in an inverse direction to those of the potential. The final sharp rise in the curves represents a range where the oxide is either not formed or is destroyed as soon as formed and no polarising effect occurs.

Summary.

(1) The formation of diethyl succinate on electrolysis of potassium ethyl malonate is shown to be an oxidation reaction and to take place only when the anode is of a suitable material and when its potential exceeds 2·3—2·4 volts referred to the normal hydrogen electrode as standard. The results are in general agreement with the views expressed by Gibson.

(2) Grey platinum resembles smooth platinum in its behaviour as electrode material.

(3) With platinised platinum and with gold anodes no synthesis occurs; but whereas the former at a potential of 3·3 causes a large oxidation of the electrolyte to carbon dioxide and water, with the latter little oxidation occurs even at potentials over 6.

(4) What appears to be complete oxidation of a portion of the electrolyte occurs with all the anode materials used, even at very low potentials. The extent of this oxidation is small with platinised platinum and gold, more considerable with smooth platinum and grey platinum.

(5) With gold a peculiar instability is observed, and an explanation of this is suggested.

My thanks are due to Professor Sir James Walker, F.R.S., for suggesting the lines of this research, and for helpful criticism during its performance.

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CCLXXXII.—*The Reaction of Bromine with Aliphatic Acids. Catalytic Effect of Acyl Halides.*

By HERBERT BEN WATSON.

THE investigation of the mechanism of the α-bromination of aliphatic acids originated in the isolation by Steiner (*Ber.*, 1874, **7**, 184) of a red additive compound of acetic acid, bromine, and hydrogen bromide, which decomposed in absence of water to give hydrogen bromide and monobromoacetic acid, and the accelerating effect of hydrogen bromide was interpreted by Hell and Mühlhäuser (*Ber.*, 1879, **12**, 727) on the hypothesis that bromination was preceded by the formation of a compound of this type. Hell and Urech (*Ber.*, 1880, **13**, 531) showed that, although the velocity of bromination is dependent on the concentration of bromine, the reaction is not of the simple bimolecular type, an initial period of very low velocity being followed by a comparatively rapid disappearance of the halogen; and they regarded this observation as confirmation of Hell and Mühlhäuser's hypothesis.

The rapid bromination of aliphatic acids in presence of phosphorus or sulphur (Hell, *Ber.*, 1881, **14**, 891; Volhard, *Annalen*, 1888, **242**, 141; Zelinsky, *Ber.*, 1887, **20**, 2026) was regarded originally as involving complete conversion of the acid into acid bromide, followed by bromination of the latter, but this interpretation is not applicable to cases where a very marked acceleration results from the presence of quantities of phosphorus or sulphur which are insufficient for any large conversion (*e.g.*, Gorodetzky and Hell, *Ber.*, 1888, **21**, 1729; Ward, J., 1922, **121**, 1161).

A new view of the reaction was put forward by Lapworth (J., 1904, **85**, 41). He observed that hydrogen chloride, as well as hydrogen bromide, has a catalytic effect, and he regarded this action as being of the same nature as the influence of acids on keto-enol changes; accordingly, he suggested that the bromination of carboxylic acids, like that of acetone, involves a relatively slow catalysed change to the enolic form, followed by instantaneous addition of

bromine at the point of unsaturation, and finally by loss of hydrogen bromide.

$$R{\cdot}CH_2{\cdot}CO_2H \xrightarrow{\text{catalyst}} R{\cdot}CH{:}C\begin{matrix}OH\\OH\end{matrix} \xrightarrow{Br_2} R{\cdot}CHBr{\cdot}C\begin{matrix}Br\\OH\\OH\end{matrix} \longrightarrow$$

$$R{\cdot}CHBr{\cdot}CO_2H + HBr.$$

He attributed the catalytic influence of *small* quantities of phosphorus to the formation of hydrogen bromide by the action of the phosphorus bromides on traces of water present or on the acid itself. This " enolic form theory " was adopted by Aschan (*Ber.*, 1912, **45**, 1913) to explain the production of brominated acid bromide and brominated acid chloride when bromine reacts with an acid chloride : but Meyer (*Ber.*, 1912, **45**, 2868) pointed out that such an interpretation is unnecessary, since the observation is explained equally well by assuming substitution followed by a reaction of hydrogen bromide with the brominated acid chloride (compare Staudinger and Anthes, *Ber.*, 1913, **46**, 1417). The results of an investigation of the bromination of acids in presence of small quantities of phosphorus were interpreted by Ward (*loc. cit.*) on the basis of Lapworth's suggestion, but he points out (J., 1923, **123**, 2212) that the theory demands the existence of carboxylic acids in a form which is neither observed nor indicated in other reactions : in the case of ketones, aldehydes, and compounds containing the $-CO{\cdot}CH_2{\cdot}CO-$ grouping where the theory has been applied successfully (Lapworth, J., 1904, **85**, 30; Dawson and Leslie, J., 1909, **95**, 1880; Dawson, Burton, and Ark, J., 1914, **105**, 1275; Meyer, *Annalen*, 1911, **380**, 235; *Ber.*, 1912, **45**, 2867; West, J., 1924, **125**, 1277), the existence of an enolide is indicated in other reactions.

The very powerful accelerating effect of a small quantity of acetic anhydride on the chlorination of acetic acid was observed by Hentschel (*Ber.*, 1884, **17**, 1286), and is now utilised in the industrial preparation of monochloroacetic acid. Hentschel postulated a pair of alternating reactions of the following type,

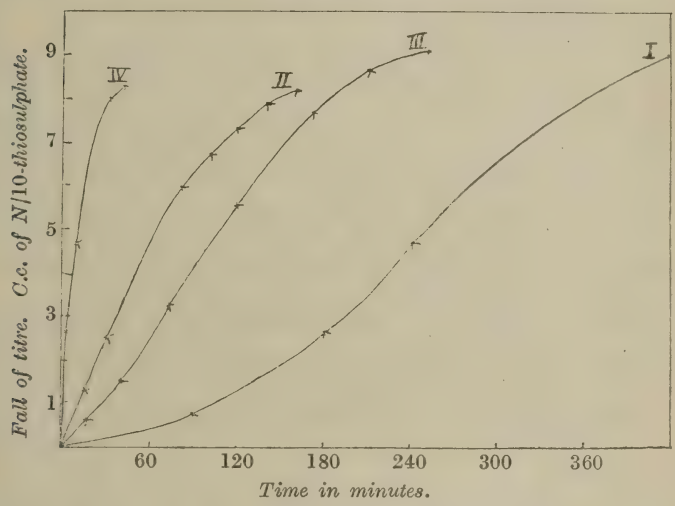
$$(CH_3{\cdot}CO)_2O + Cl_2 = CH_2Cl{\cdot}CO_2H + CH_3{\cdot}COCl \quad . \quad . \quad . \quad . \quad (1)$$

$$CH_3{\cdot}COCl + CH_3{\cdot}CO_2H = (CH_3{\cdot}CO)_2O + HCl \quad . \quad . \quad . \quad . \quad (2)$$

The individual reactions (1) and (2) had been observed by Gal (*Ann. Chim. Phys.*, 1869, **66**, 187) and Anschütz (*Annalen*, 1884, **226**, 1). Shaw (J., 1923, **123**, 2233) found that acetic anhydride similarly accelerates the bromination of acetic and homologous acids, and suggested that bromination may take place either (*a*) through the preliminary enolisation of the acid, or (*b*) through a series of changes involving acetic anhydride, similar to those postulated by Hentschel, the latter course being by far the more rapid.

A re-examination of the action of bromine on acetic, propionic, and *n*-butyric acids at 100° has been undertaken by the author, and the results are summarised in the following.

(a) *Catalytic Effect on Halogen Acids.*—When no catalyst is present initially, the course of the reaction indicates autocatalysis by the hydrogen bromide formed (see curve I): a "period of acceleration" is followed by the attainment of a maximum velocity, and the reaction then becomes steadily slower: variation in the initial concentration of bromine has a marked effect (compare Hell and Urech, *loc. cit.*). If hydrogen bromide is present initially, the



Acetic acid and bromine. Initial $[Br_2] = 0{\cdot}24\,M$.

I. *No added catalyst.* II. HBr *introduced* (0·268 *M*).
III. HCl *introduced* (0·317 *M*). IV. AcBr *introduced* (0·047 *M*).

reaction proceeds more quickly: a very small quantity of the halogen acid reduces the period of acceleration to a marked extent, and in presence of a moderate initial concentration of hydrogen bromide (0·2*M*) this period disappears (see curve II). The velocity is thus dependent on the concentration of bromine and that of hydrogen bromide: no simple mathematical relationship has been found for acetic and *n*-butyric acids, but in the case of propionic acid, when the acid is present in large excess, the velocity is represented with a tolerable degree of accuracy by the expression $v = k[Br_2][HBr]^{\frac{1}{2}}$. This expression holds over a wide range of concentration of hydrogen bromide extending from zero to molar (see Table II): when, however, the concentration of the halogen acid is very great (2*M*), a retarding influence comes into play.

This is undoubtedly due to perbromide formation, as indicated by the pale colour of the reaction mixture (compare Joseph and Jinendradasa, J., 1911, **99**, 274), a similar retardation having been observed in other reactions (Bugarsky, *Z. physikal. Chem.*, 1901, **38**, 561; 1904, **48**, 63; Bognar, *ibid.*, 1910, **71**, 529; Orton and Jones, *Rep. Brit. Assoc.*, 1910, 99). Hydrogen chloride also exerts a catalytic effect (compare Lapworth, Shaw), but is somewhat less effective than hydrogen bromide, and when it is present even at saturation the initial period of acceleration does not disappear completely (see curve III). The velocity does not remain constant as stated by Shaw (*loc. cit.*), who apparently took an insufficient number of points on the curve.

In order to determine whether this catalytic action is common to all acids, the effect of small quantities of trichloroacetic and sulphuric acids was examined. The effect of trichloroacetic acid is scarcely perceptible (see Table 1, *a* and *b*) : sulphuric acid also has but little effect, but the bromination is here complicated by side reactions. The marked catalytic effect of halogen acids is clearly specific, and not common to acids in general, and this fact together with the dependence of the velocity on the concentration of bromine is evidence against the validity of the " enolic form theory."

(b) *Catalytic Effect of Acetyl Bromide.*—The very powerful acceleration produced by the presence of a small quantity of acetic anhydride was observed by Shaw (*loc. cit.*), and a fuller investigation of this reaction at 100° has established the following facts (the acetic acid used contained 0·1% of water, and in all cases was present in very great excess) :

(1) If the anhydride is not in excess of the water present in the acid, no catalytic effect is observed.

(2) When the anhydride is in excess of the water, a short period of acceleration (which escaped Shaw's notice) is followed by a rapid reaction : after the initial period, the velocity is proportional to the concentration of bromine, and varies directly and almost proportionately with that of the anhydride (see Tables IV and V). The effect of acetic anhydride, as compared with that of halogen acids, is seen from the following :

Catalyst added.	No catalyst.	HBr = 0·053*M*.	HCl = 0·063*M*.	Ac_2O = 0·05*M*.
Initial titre (N/10-$Na_2S_2O_3$) ...	9·48	9·58	10·02	9·25
Fall of titre in 45 mins.	0·25	1·55	0·78	9·05

(3) If hydrogen bromide, in excess of the anhydride, is also introduced, the initial period of acceleration disappears, and the velocity is proportional to the concentration of bromine from the commencement. The actual value of k_1 is somewhat smaller than in (2), and

becomes very considerably smaller when the concentration of hydrogen bromide is high (see Table VI). This may be attributed to perbromide formation, which is indicated by the colour of the reaction mixture : such combination becomes more extensive as the water content of acetic acid diminishes (Jones, J., 1911, **99**, 402). A slight falling off in the value of k_1 towards the end of the reaction, which was observed in some of the experiments, is probably due to the same cause.

(4) The presence of hydrogen chloride in excess of the anhydride does not destroy the catalytic effect of the latter, as stated by Shaw (*loc. cit.*), but exerts a comparatively small retarding influence. Here again, after the initial period, the velocity is proportional to the concentration of bromine (see Table VII).

It is suggested that these results are best interpreted as follows : when a mixture of acetic acid, bromine, and acetic anhydride is heated at 100°, the anhydride not being in excess of the water present in the acid, complete and relatively instantaneous hydrolysis of the anhydride takes place, and no acceleration is observed. If the anhydride be in excess of the water, the first reaction consists in an immediate removal of water by hydrolysis of the equivalent quantity of anhydride. The remainder then reacts with bromine, $(CH_3{\cdot}CO)_2O + Br_2 = CH_2Br{\cdot}CO_2H + CH_3{\cdot}COBr$ (Gal, *loc. cit.*) : with the quantities of anhydride employed in the investigation, the percentage of the total bromine required for this reaction is small, being equivalent to about 0·5 c.c. of N/10-thiosulphate. The conclusion is thus reached that the observed acceleration is due to the presence of acetyl bromide. If this be the case, the velocity will reach its maximum value only when the bromination of the anhydride is complete, and thus the period of acceleration is accounted for. In presence of the more powerful catalyst the influence of the hydrogen bromide formed is inappreciable (or perhaps is balanced by perbromide formation), and there is no apparent autocatalysis : the reaction therefore follows the first order. If hydrogen bromide is present initially in excess of the anhydride, it reacts with great speed according to the equation $(CH_3{\cdot}CO)_2O + HBr = CH_3{\cdot}CO_2H + CH_3{\cdot}COBr$ (compare Gal, *loc. cit.*, on the reaction of hydrogen chloride with acetic anhydride). The acid bromide is then present from the commencement at its maximum concentration, and there is no period of acceleration.

In order to obtain direct evidence of the accelerating influence of acetyl bromide, the bromination of acetic acid in presence of varying small quantities of the acid bromide (introduced as such) was studied ; the results confirmed the hypothesis outlined above (see Tables VIII and IX). When the acetyl bromide is not in

excess of the water present in the acid, the reaction follows, as would be expected, the same course as when hydrogen bromide alone is introduced, while the acid bromide, present in excess of the water, is an exceedingly powerful catalyst * (see curve IV). Its effect is similar to that of the anhydride at equivalent concentration save that (*a*) the velocity is now proportional to the concentration of bromine from the commencement, and (*b*) the values of k_1 are somewhat lower (perbromide formation), and in agreement with the values obtained in presence of acetic anhydride and hydrogen bromide in conjunction. Measurements employing varying initial quantities of the catalyst showed that the velocity is proportional to the concentration of acetyl bromide (see Table X).

Acetyl bromide exerts a similar influence on the bromination of other aliphatic acids. The effect of acetic anhydride on the bromination of the homologues of acetic acid was observed by Shaw (*loc. cit.*), and the author has shown that acetic anhydride and acetyl bromide accelerate the bromination of propionic and *n*-butyric acids in a manner exactly similar to that described for acetic acid.

Examination of the effect of acetyl chloride has shown that if the acid chloride is not in excess of the water present it produces the same effect as does hydrogen chloride, while if it is in excess of the water the bromination is initially much faster than in presence of halogen acids, but less rapid than in presence of acetyl bromide : when sufficient hydrogen bromide has been produced to bring about complete conversion of the acid chloride to acid bromide ($CH_3 \cdot COCl + HBr \rightleftharpoons CH_3 \cdot COBr + HCl$, Staudinger and Anthes, *loc. cit.*) a rapid first-order reaction takes place : the actual value of k_1 is the same as when acetic anhydride is initially present and somewhat greater than when acetyl bromide is introduced initially (less " fixing " of bromine as perbromide). Acetyl chloride is thus a less powerful catalyst than acetyl bromide. The retarding in-

* An anomalous result obtained by Ward (J., 1922, **121**, 1164) receives a simple interpretation in the light of this fact. He found that acetic acid, previously saturated with hydrogen bromide, did not react completely with a molecular proportion of bromine after heating at 100° for *three* hours, and this observation is in harmony with the results of Lapworth (*loc. cit.*) and of the author. On the other hand, when he introduced acetyl bromide for the purpose of dehydrating the acid and at the same time providing halogen acid, he carried out the bromination in *one* hour. The amount of acetyl bromide added (3 g. to 50 g. of acetic acid) was equivalent to the water content of an acid having 0·878% of water (m. p. rather above 15°). Ward's acid had been purified by freezing, and it is unlikely that it contained such a high percentage of water. The indications are that the acetyl bromide was in excess of the water, and that its presence was responsible for the rapid bromination.

fluence of an excess of hydrogen chloride on the bromination in presence of acetic anhydride may then be attributed to the formation of acid chloride from the anhydride $(CH_3{\cdot}CO)_2O + HCl = CH_3{\cdot}CO_2H + CH_3{\cdot}COCl$ (Gal, *loc. cit.*); complete conversion of acid chloride into acid bromide during the reaction is here prevented by the excess of hydrogen chloride, and hence the comparatively small value of k_1.

(c) *Catalytic Effect of Acid Bromides in General.*—Investigation of the bromination of acetic and propionic acids in presence of bromoacetyl, propionyl, and benzoyl bromides has revealed the fact that the introduction of any one of these acid bromides brings about an acceleration identical with that which is produced by acetyl bromide at equivalent concentration. The velocity is proportional to the concentration of bromine and of acid bromide, and the values of k_1 are the same in each case (see Tables X and XI).

The introduction of benzoyl chloride into a reaction mixture of bromine and acetic acid produces an effect which is similar to that of acetyl chloride at equivalent concentration, except that the velocity is slightly less (see Table XII).

Discussion of Results.

1. The peculiar catalytic influence of *acid bromides* on the bromination of aliphatic acids may possibly involve the following steps. The acid bromide is first brominated,

$$R{\cdot}CH_2{\cdot}COBr + Br_2 = R{\cdot}CHBr{\cdot}COBr + HBr \quad . \quad . \quad . \quad (1)$$

The aliphatic acid (present in very great excess) then reacts with the brominated acid bromide,

$$R{\cdot}CHBr{\cdot}COBr + R{\cdot}CH_2{\cdot}CO_2H = R{\cdot}CH_2{\cdot}COBr + R{\cdot}CHBr{\cdot}CO_2H \quad (2)$$

the final product being the brominated acid, and the acyl bromide going through the same series of changes again.

The results of Urech (*Ber.*, 1880, **13**, 1688) indicate that the bromination of acetyl bromide is a reaction of the second order; in the scheme outlined above, the concentrations of acid bromide and brominated acid bromide remain constant during the reaction, while that of the acid is very large; for a given initial concentration of acid bromide, therefore, the velocity will vary only as the concentration of bromine, but will be proportional to the initial concentration of acid bromide. This is in complete agreement with the observed facts.

If the bromide of a different carboxylic acid be present initially, an exactly similar acceleration is observed, and a similar mechanism is thus indicated. This is interpreted most simply by supposing that reactions (1) and (2) above are preceded by

$$R'{\cdot}COBr + R{\cdot}CH_2{\cdot}CO_2H = R{\cdot}CH_2{\cdot}COBr + R'{\cdot}CO_2H,$$

which is exactly similar in character to reaction (2). This idea is in harmony with the observation of Polzenius (*Chem. Ztg.*, 1896, **20**, 46) that benzoyl chloride and acetic acid when heated together yield benzoic acid and acetyl chloride, whilst a similar reaction was suggested by Orton (J., 1901, **79**, 1351) as providing a possible explanation of the formation of acid amides by the reaction of benzoyl chloride with carboxylic acids in presence of ammonia.

The catalytic action of acid bromides cannot be interpreted by postulating the intermediate formation of the acid anhydride (compare Shaw, *loc. cit.*) or of a mixed anhydride, for an initial period of low velocity is observed when the anhydride is introduced, but not when the acid bromide is present initially.

2. *Acid chlorides* are less powerful catalysts than acid bromides, but their effect may be interpreted in a similar manner by postulating the reactions

$$R'\cdot COCl + R\cdot CH_2\cdot CO_2H = R\cdot CH_2\cdot COCl + R'\cdot CO_2H,$$
$$R\cdot CH_2\cdot COCl + Br_2 = R\cdot CHBr\cdot COCl + HBr,$$
$$R\cdot CHBr\cdot COCl + R\cdot CH_2\cdot CO_2H = R\cdot CH_2\cdot COCl + R\cdot CHBr\cdot CO_2H.$$

It must be assumed that one or more of these reactions proceed less rapidly than the corresponding reactions involving the acid bromide. The hydrogen bromide formed in the reaction, however, now reacts with the acid chloride (or brominated acid chloride), and the above reactions are gradually replaced by those in which the acid bromide takes part (compare Staudinger and Anthes, *loc. cit.*). The velocity ultimately attained will depend on the proportion of acid bromide or brominated acid bromide present in the equilibrium $R\cdot CH_2\cdot COCl + HBr \rightleftharpoons R\cdot CH_2\cdot COBr + HCl$ or the equilibrium $R\cdot CHBr\cdot COCl + HBr \rightleftharpoons R\cdot CHBr\cdot COBr + HCl$, and is not likely to be identical for all acid chlorides. This is in harmony with experimental results.

3. The accelerating effect of a small amount of *phosphorus* (Hell-Volhard-Zelinsky reaction) is now interpreted simply. The bromination of acetic acid at 100° in presence of a halogen acid is a slow process requiring at least *six* hours for completion (Lapworth, Ward; compare the author's results, Tables I to III), whilst in presence of a very small amount of phosphorus the reaction is complete in *one* hour (Ward, J., 1922, **121**, 1163). The catalytic effect of phosphorus is thus much more powerful than that of halogen acids, but is of the same order of magnitude as the effect of acid bromides. Moreover, the bromination in presence of phosphorus always results in the formation of a small quantity at least of acid bromide or brominated acid bromide (Ward), and it seems obvious that the acceleration is to be attributed to this small quantity of acid bromide.

4. *Halogen acids.* It may be further suggested that the effect of halogen acids is due to traces of the acid halides present in equilibrium with the aliphatic acid, $R{\cdot}CO_2H + HX \rightleftharpoons R{\cdot}COX + H_2O$. The very different effects of halogen acids and acyl halides indicate that the quantity of acyl halide necessary to produce the observed velocity would be too small for detection, and the existence of such an equilibrium has never been demonstrated. It is not impossible, however, in view of the reversible nature of the hydrolysis of many inorganic chlorides, while it is suggested by reactions of the type $R{\cdot}CN + R'{\cdot}CO_2H + 2HCl = R{\cdot}CO{\cdot}NH_2,HCl + R'{\cdot}COCl$ (Colson, *Compt. rend.*, 1895, **121**, 1155). An interpretation of this type is supported by the following facts : (*a*) the influence of halogen acids is specific, and not common to acids in general; (*b*) Lapworth (J., 1904, **85**, 41) observed that a small quantity of water (which would displace the above equilibrium towards the left-hand side, thus reducing the concentration of acyl halide) reduced very considerably the speed of bromination, and this result has been confirmed by the author; (*c*) when varying amounts of the acid bromide (producing the above equilibrium) are added, there is a continuous increase in velocity as the amount of acid bromide becomes greater, and not a sudden increase at the point where the bromide is just in excess of the water (see Table VIII), whilst, on the other hand, addition of anhydride causes a sudden increase at this point (see Table IV); in the former case, therefore, a gradual increase in the amount rather than a sudden change in the nature of the catalyst is indicated.

The above suggestion, by postulating a similar mechanism in every case, brings into harmony all previous observations of the catalysed bromination of aliphatic acids.

In ascribing the rapid bromination to an initial interaction of bromine with the acyl bromide, no hypothesis is at present put forward as to the stages of this reaction, but it is possible that the acyl bromide " enolises " or passes into an " active " state more readily and rapidly than the acid. In that case, the reaction would be the result of a *rapid* enolisation followed by a *slow* reaction with bromine,

$$R{\cdot}CH_2{\cdot}COBr \xrightarrow{\text{rapid}} R{\cdot}CH{:}C\begin{matrix}OH\\Br\end{matrix} \xrightarrow[Br_2]{\text{slow}} R{\cdot}CHBr{\cdot}C\begin{matrix}Br\\Br\\OH\end{matrix} \xrightarrow{\text{rapid}} R{\cdot}CHBr{\cdot}COBr + HBr$$

compare West, J., 1924, **125**, 1282). In such a suggestion α-bromination finds an easy explanation.

Experimental.

The acetic acid used throughout the investigation, except where otherwise indicated, melted at 16·4° (H_2O = 0·1%). All specimens of Kahlbaum's " 100% acetic acid " examined were completely free from impurities which react with bromine at the ordinary temperature : in some cases, this acid melted at 16·4°, and was used without fractionation, while from specimens of lower melting point (16 — 16·2°) good yields of acid melting at 16·4° were obtained by fractional distillation through an eight-pear still-head. Post-war acetic acids of British manufacture which were not stable to bromine at the ordinary temperature were purified by distillation from chromic anhydride (Orton and Bradfield, J., 1924, **125**, 960) followed by fractionation. The propionic and *n*-butyric acids were prepared by distillation of " Kahlbaum " acid, the fractions used boiling respectively at 140·8—141°/764 mm. and 162·2—162·3°/766 mm. Solutions of bromine in these acids showed no appreciable fall of thiosulphate titre after several days at 25°. The bromine was shaken three times with an equal volume of water, dried under concentrated sulphuric acid, and finally separated and distilled from a little barium carbonate in an all-glass apparatus.

The method employed in the velocity measurements was similar to that of Hell and Urech (*loc. cit.*) and of Shaw (*loc. cit.*). A reaction mixture was made up containing the aliphatic acid, bromine, and the catalyst in the desired proportions, the aliphatic acid always being in large excess. The thiosulphate titre of 2 c.c. was determined, and portions of 2 c.c. were then introduced into small tubes : the tubes were sealed immediately, and immersed in a bath of boiling water. At given intervals tubes were withdrawn, broken under aqueous potassium iodide, and the iodine was titrated against standard thiosulphate. The figures in the tables which follow refer to c.c. of N/10-thiosulphate : time is stated throughout in minutes.

Catalytic Effect of Halogen Acids.

Solutions of hydrogen bromide in the aliphatic acids were prepared by dropping aqueous hydrobromic acid (*d* 1·7) on to phosphorus pentoxide, and passing the evolved gas over moist red phosphorus then over phosphorus pentoxide, and finally into the aliphatic acid. The solutions of hydrogen chloride were obtained by dropping pure concentrated hydrochloric acid into pure concentrated sulphuric acid, and passing the gas liberated over calcium chloride and then into the aliphatic acid. The concentrations of the solutions were determined by precipitation as silver bromide or chloride, and the required volumes were introduced into different reaction mixtures

TABLE I.

Acetic Acid and Bromine.

(*a*) No added catalyst.

I.		II.		III.	
Time.	Titre.	Time.	Titre.	Time.	Titre.
0	18·70	0	9·48	0	5·20
60	18·15	90	8·68	60	4·62
120	17·35	180	6·82	120	3·75
210	14·55	240	4·75	240	1·22
270	10·00	270	3·48	300	0·48
330	6·35	300	2·85		
480	0·72	330	2·10		
		420	0·45		

(*b*) $CCl_3 \cdot CO_2H$ as catalyst.

$[CCl_3 \cdot CO_2H] = 0{\cdot}206M.$

Time.	Titre.
0	9·40
90	8·25
180	5·90
210	4·95
240	3·60
270	2·65
300	1·88
360	0·82

(*c*) Hydrogen bromide as catalyst.

I. Initial [HBr] = 0·268*M*.		II. Initial [HBr] = 0·268*M*.		III. Initial [HBr] = 0·053*M*.	
Time.	Titre.	Time.	Titre.	Time.	Titre.
0	18·08	0	9·48	0	9·58
15	16·32	10	8·62	10	9·12
30	14·42	15	8·18	20	8·95
45	12·35	30	6·92	40	8·25
60	10·22	40	6·12	80	6·55
100	5·72	60	4·78	140	3·75
140	3·25	80	3·62	200	1·70
180	1·72	100	2·80	260	0·65
230	0·78	120	2·15		
		140	1·65		
		160	1·20		

(*d*) Hydrogen chloride as catalyst.

I. [HCl] = 0·317*M*.		II. [HCl] = 0·317*M*.		III. [HCl] = 0·063*M*.		IV. [HCl] = 1·78*M*.	
Time.	Titre.	Time.	Titre.	Time.	Titre.	Time.	Titre.
0	17·18	0	9·92	0	10·02	0	9·52
10	16·85	15	9·28	15	9·78	20	8·05
20	16·45	40	8·38	30	9·50	45	6·15
50	14·45	75	6·58	60	9·05	90	3·48
80	13·22	100	5·22	120	7·55	120	2·95
110	10·58	120	4·42			210	0·68
140	8·98	140	3·40				
250	2·55	170	2·20				
		210	1·28				
		250	0·70				

Effect of Acetic Anhydride.

Acetic Acid and Bromine.—(a) *Presence of acetic anhydride alone.* The acetic anhydride was purified by redistillation through an eight-pear still-head, as described by Orton and Jones (J., 1912, 101, 1720). Mixtures of acetic acid (m. p. 16·4°), bromine, and varying small quantities of the anhydride were made up, and the

Table II.

Propionic Acid and Bromine.

Values of k are calculated from the formula $v = k[Br_2][HBr]^{\frac{1}{2}}$. If a be the initial concentration of hydrogen bromide, and b the initial concentration of bromine, this becomes $v = k(b - x)(a + x)^{\frac{1}{2}}$, which on integration gives,

$$kt = \frac{1}{\sqrt{b+a}}\left[\log_e\frac{\sqrt{b+a}+\sqrt{a+x}}{\sqrt{b+a}-\sqrt{a+x}} - \log_e\frac{\sqrt{b+a}+\sqrt{a}}{\sqrt{b+a}-\sqrt{a}}\right].$$

(*a*) No added catalyst.

I.			II.		
Time.	Titre.	k.	Time.	Titre.	k.
0	16·70	—	0	9·85	—
64	15·78	0·0113	60	9·60	0·0116
150	14·32	0·0082	90	9·32	0·0105
210	12·92	0·0077	120	9·05	0·0093
270	9·70	0·0088	150	8·78	0·0104
300	7·98	0·0094	240	7·40	0·0092
360	4·28	0·0112	300	6·52	0·0089
420	2·62	0·0116	390	3·95	0·0106
480	1·12	0·0131	420	3·52	0·0106
			510	1·40	0·0128

(*b*) Hydrogen bromide as catalyst.

I. Initial [HBr] = 0·0442M.			II. Initial [HBr] = 0·4455M.		
Time.	Titre.	k.	Time.	Titre.	k.
0	10·22	—	0	11·18	—
28	9·55	0·0107	15	9·95	0·0107
90	8·35	0·0087	30	8·65	0·0119
215	4·55	0·0112	45	7·45	0·0126
270	2·68	0·0132	60	6·42	0·0128
330	1·20	0·0143	75	5·28	0·0137
			90	4·38	0·0140
			105	3·70	0·0140
			125	2·68	0·0150

III. Initial [HBr] = 0·8908M.			IV. Initial [HBr] = 2·21M.		
0	11·00	—	0	10·75	—
15	9·65	0·0092	33	8·30	0·0052
30	8·32	0·0096	84	5·35	0·0056
45	6·95	0·0105	210	1·75	0·0059
60	5·80	0·0107			
75	4·98	0·0107			
90	4·00	0·0115			
120	2·80	0·0111			
150	1·75	0·0094			
180	1·25	0·0114			

course of the bromination was followed as described above. In tw experiments the anhydride was insufficient to react with the whol of the water present in the acid, whilst in the remaining three i was in excess. The results obtained are indicated in Tables IV and V.

Table III.

n-Butyric Acid and Bromine.

(*a*) No added catalyst. (*b*) Hydrogen bromide as catalyst.

		I. Initial [HBr] = 0·2738*M*.		II. Initial [HBr] = 0·8215*M*.	
Time.	Titre.	Time.	Titre.	Time.	Titre.
0	9·28	0	10·28	0	9·48
60	8·12	15	9·75	10	8·98
180	5·45	30	9·25	20	8·35
240	4·30	60	8·25	30	7·85
300	3·82	120	6·32	60	6·38
360	2·75	240	3·05	90	5·15
420	1·65	390	0·92	120	4·02
				150	3·25
				180	2·45

Table IV.

	A.	B.	C.	D.	E.	F.
Grams Ac_2O added in 25 c.c.	0	0·0558	0·1104	0·1637	0·2334	0·2732
% water remaining after hydrolysis of Ac_2O	0·10	0·062	0·025	0	0	0
Conc. of Ac_2O in excess of water	0	0	0	0·007	0·03	0·05*M*
Initial titre (N/10-$Na_2S_2O_3$)	9·48	9·42	9·45	9·45	9·45	9·25
Fall of titre in 20 mins.	0·05	0·15	0·20	1·50	4·03	6·97
Fall of titre in 45 mins.	0·25	0·45	0·48	5·90	8·15	9·05

Table V.

Values of $k_1 = \frac{1}{t_2 - t_1} \cdot \log_e \frac{a - x_1}{a - x_2}$ for reactions E and F above.

E. $[Ac_2O] = 0·03M$. $t_1 = 15$.			F. $[Ac_2O] = 0·05M$. $t_1 = 10$.			F′. $[Ac_2O] = 0·05M$. $t_1 = 10$.		
Time.	Titre.	k_1.	Time.	Titre.	k_1.	Time.	Titre.	k_1.
0	9·45		0	9·25		0	13·75	
5	9·25		5	9·15		5	13·40	
10	8·62		10	6·98		10	9·92	
15	7·08		15	4·20	0·101	15	5·20	0·129
20	5·42	0·053	20	2·28	0·112	20	3·05	0·118
25	3·98	0·057	25	1·42	0·106	25	2·05	0·104
30	3·32	0·051	30	0·85	0·106	30	1·35	0·100
35	2·28	0·056	35	0·58	0·100	40	0·65	0·091
40	1·75	0·055						
45	1·30	0·056						
55	1·02	0·048						
	Mean	0·054		Mean	0·105		Mean	0·108

(b) *Presence of acetic anhydride and hydrogen bromide in conjunction*

TABLE VI.

$[Ac_2O] = 0{\cdot}05M$. (Compare F and F′, Table V.)

Values of $k_1 = 1/t \,.\, \log_e a/a - x$.

I. $[HBr] = 0{\cdot}1065M$.			II. $[HBr] = 0{\cdot}2683M$.			III. $[HBr] = 1{\cdot}3M$.		
Time.	Titre.	k_1.	Time.	Titre.	k_1.	Time.	Titre.	k_1.
0	13·68		0	13·40		0	13·95	
5	8·98	0·076	15	5·15	0·064	10	12·12	0·014
7	8·15	0·074	25	2·95	0·060	20	10·10	0·016
10	6·25	0·078	35	1·78	0·057	30	8·62	0·016
15	4·32	0·077	45	1·10	0·056	50	6·05	0·017
30	1·65	0·071	55	0·70	0·054	90	3·15	0·016
50	0·58	0·063						
	Mean	0·073		Mean	0·058		Mean	0·016

(c) *Presence of acetic anhydride and hydrogen chloride in conjunction*

TABLE VII.

$[Ac_2O] = 0{\cdot}05M$. (Compare F and F′, Table V.)

Values of $k_1 = \dfrac{t}{t_2 - t_1} \,.\, \log_e \dfrac{a - x_1}{a - x_2}$. $t_1 = 10$ mins.

I. $[HCl] = 0{\cdot}317M$.			II. $[HCl] = 1{\cdot}57M$.		
Time.	Titre.	k_1.	Time.	Titre.	k_1.
0	13·35		0	14·20	
5	12·38		5	12·40	
10	10·48		10	10·55	
15	8·25	0·047	20	6·92	0·042
20	6·25	0·051	30	4·48	0·043
30	3·80	0·051	45	2·10	0·046
	Mean	0·050		Mean	0·044

Effect of Acetyl Bromide.

The acetyl bromide was purified from dissolved halogen acid by bubbling dried air through the liquid under reduced pressure, and then fractionally distilled. Reaction mixtures of acetic acid, bromine, and varying small quantities of the acid bromide were made up and treated as before. The results are indicated in Tables VIII and IX.

TABLE VIII.

	A.	B.	C.	D.
Grams AcBr added in 25 c.c.	0·0892	0·1518	0·2157	0·3212
% water remaining after hydrolysis of AcBr	0·050	0·014	0	0
Conc. of AcBr in excess of water	0	0	trace	0·047
[HBr] formed by hydrolysis of AcBr ...	0·029M	0·049M	0·058M	0·058M
Initial titre (N/10-$Na_2S_2O_3$)	9·35	9·32	9·38	9·55
Fall of titre in 20 mins.	0·35	0·82	2·25	6·90
Fall of titre in 30 mins.	0·70	1·42	3·20	8·00

Table IX.

Values of $k_1 = 1/t \cdot \log_e a/a - x$ for reaction D above.
[AcBr] = 0·047M.

Time	0	5	8	10	15	20	30	
Titre	9·55	6·95	5·65	4·92	3·60	2·65	1·55	Mean
k_1 ...		0·064	0·064	0·066	0·065	0·063	0·061	0·064

Comparison of Effects of Different Acid Bromides.

Pure acetyl bromide was obtained as already described. Propionyl, benzoyl, and bromoacetyl bromides were prepared by treatment of propionic, benzoic, and acetic acids respectively with the required quantities of red phosphorus and bromine. The product was distilled from the phosphorus compounds under reduced pressure, and finally fractionated at ordinary pressure (compare Claisen, *Ber.*, 1881, **14**, 2473; Auwers and Bernhardt, *Ber.*, 1891, **24**, 2219). Reaction mixtures containing acetic or propionic acid (in large excess), bromine, and equivalent quantities of the different acid bromides were made up, and the reaction at 100° followed as before.

Table X.

Acetic Acid and Bromine.

M. p. of acetic acid 16·48° (% H_2O = 0·06).
Values of $k_1 = 1/t \cdot \log_e a/a - x$.

$CH_3 \cdot COBr$ = 0·0745M.		$CH_3 \cdot CH_2 \cdot COBr$ = 0·0745M.		$C_6H_5 \cdot COBr$ = 0·0745M.		$CH_2Br \cdot COBr$ = 0·0727M.	
Time.	Titre. k_1.	Time.	Titre. k_1.	Time.	Titre. k_1.	Time.	Titre. k_1
0	9·10	0	8·98	0	9·38	0	9·25
3	6·92 0·092	3	6·88 0·089	3	7·00 0·098	3	7·18 0·085
6	4·95 0·101	6	4·75 0·105	6	4·78 0·112	6	5·25 0·094
9	3·68 0·100	9	3·40 0·107	9	3·52 0·109	9	3·82 0·098
12	2·88 0·096	12	2·58 0·104	12	2·68 0·104	12	2·95 0·095
15	2·15 0·096	15	1·92 0·102	15	2·15 0·098	15	2·35 0·091
20	1·38 0·094	20	1·22 0·100	20	1·35 0·097	20	1·62 0·087
25	0·95 0·089	25	0·75 0·099	25	0·92 0·092		
	Mean 0·096		Mean 0·101		Mean 0·101		Mean 0·092

$CH_3 \cdot COBr$ = 0·0527M.		$CH_3 \cdot CH_2 \cdot COBr$ = 0·0527M.		$C_6H_5 \cdot COBr$ = 0·0527M.	
Time.	Titre. k_1.	Time.	Titre. k_1.	Time.	Titre. k_1.
0	9·35	0	8·05	0	9·18
5	6·68 0·067	5	5·52 0·075	5	6·32 0·074
10	4·58 0·072	10	3·62 0·080	10	4·78 0·065
15	3·15 0·073	15	2·42 0·080	15	2·85 0·077
20	2·35 0·069	20	1·65 0·078	20	2·00 0·076
25	1·75 0·067	25	1·18 0·077	25	1·52 0·072
30	1·25 0·067	30	0·80 0·076	30	1·12 0·070
35	0·95 0·065	35	0·55 0·076	35	0·80 0·069
	Mean 0·069		Mean 0·077		Mean 0·072

Summary of Table X.

Catalyst.	C.	k_1.	k_1/C.	C.	k_1.	k_1/C.
$CH_3 \cdot COBr$	0·0745	0·096	1·29	0·0527	0·069	1·31
$CH_3 \cdot CH_2 \cdot COBr$	0·0745	0·101	1·35	0·0527	0·077	1·46
$C_6H_5 \cdot COBr$	0·0745	0·101	1·35	0·0527	0·072	1·37
$CH_2Br \cdot COBr$	0·0727	0·092	1·27			

Table XI.

Propionic Acid and Bromine.

Values of $k_1 = 1/t \cdot \log_e a/a - x$.

Equivalent quantities of acid bromides present.

$CH_3 \cdot COBr$.			$CH_3 \cdot CH_2 \cdot COBr$.			$C_6H_5 \cdot COBr$.		
Time.	Titre.	k_1.	Time.	Titre.	k_1.	Time.	Titre.	k_1.
0	9·30		0	8·62		0	8·65	
5	7·95	0·032	10	6·52	0·028	5	7·22	0·036
10	7·20	0·026	15	5·75	0·027	10	6·38	0·031
15	6·20	0·027	20	4·82	0·029	15	5·15	0·034
25	4·72	0·027	25	4·32	0·028	20	4·65	0·031
45	2·18	0·032	30	3·72	0·028	30	3·40	0·031
			35	2·72	0·032			
	Mean	0·029		Mean	0·029		Mean	0·033

Comparison of Effects of Acetyl and Benzoyl Chlorides.

The acid chlorides were purified by fractional distillation, and the reaction of acetic acid and bromine in presence of equivalent quantities of each was followed as before. M. p. of acetic acid 16·4° ($H_2O = 0{\cdot}1\%$).

Table XII.

Values of $k_1 = \dfrac{1}{t_2 - t_1} \cdot \log_e \dfrac{a - x_1}{a - x_2}$. $t_1 = 6$ mins.

$CH_3 \cdot COCl = 0{\cdot}05M$.			$C_6H_5 \cdot COCl = 0{\cdot}05M$.		
Time.	Titre.	k_1.	Time.	Titre.	k_1.
0	9·38		0	9·68	
3	8·62		3	9·35	
6	6·98		6	8·08	
9	5·05	0·108	9	6·18	0·088
12	3·58	0·111	12	4·82	0·086
15	2·58	0·111	15	3·50	0·092
20	1·50	0·110	20	2·08	0·096
25	0·98	0·105	25	1·38	0·092
30	0·62	0·101	30	0·92	0·090
	Mean	0·108		Mean	0·090

In conclusion, the author wishes to express his gratitude to Professor Orton, F.R.S., who suggested the subject, for his advice and criticism during the progress of the research. The expense of the research was in part defrayed by a grant from the Chemical Society Research Fund, for which the author desires to tender his thanks.

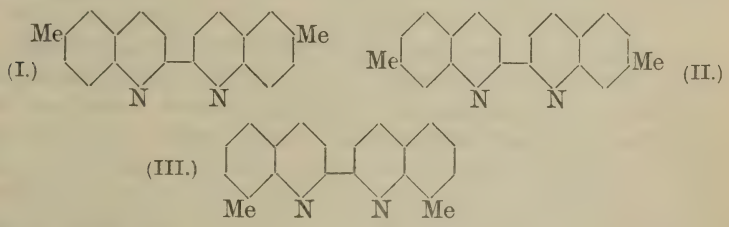
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CCLXXXIII.—*Homologues of 2 : 2′-Diquinolyl.*

By Edward John Venn Conolly.

2 : 2′-Diquinolyl was prepared by Weidel (*Monatsh.*, 1881, **2**, 491; 1886, **7**, 327) by the action of sodium on quinoline, and its constitution proved by Weidel and Strache (*ibid.*, 1886, **7**, 306) from a study of its oxidation products. The preparation of homologues from 6-, 7-, and 8-methylquinolines is described below. During this work several instances of steric hindrance were observed. Thus, under the conditions stated below, good yields of the corresponding diquinolyls (I) and (II) were obtained from 6- and 7-methylquinolines, but the yield from 8-methylquinoline was very small; the substitution of potassium for sodium did not materially alter the results. The proximity of the methyl group to the nitrogen atom in the pyridine ring therefore seems to hinder the union of the two quinolyl nuclei. Also an ethiodide of 8 : 8′-dimethyl-2 : 2′-diquinolyl (III) could not be obtained even at 180°, possibly because the tertiary nitrogen atoms are practically "di-ortho-substituted."



While attempting to prove the constitution of the diquinolyls by a Fittig-Wurtz synthesis, the method of Tschitschibabin (*Ber.*, 1923, **56**, 1879) was used for the preparation of 6-methylcarbostyril.

Experimental.

6 : 6′-Dimethyl-2 : 2′-diquinolyl (I).—6-Methylquinoline (70 g.) and sodium (7 g.) in small pieces were heated together at about 100° during 2 hours and then at 150—160° during 7 to 8 hours. The dark brown, extremely viscous product, which solidified when cooled, was triturated with dry ether; sodium was removed by means of a fine sieve, and the ethereal solution filtered. The light brown residue of crude dimethyldiquinolyl (yield 37 g.) was extracted once with alcohol (100 c.c.), which removed most of the dark coloured impurities, and the light yellow residue was then repeatedly crystallised from benzene, until constant in melting point.

The ethereal filtrate obtained above was evaporated and the oily product distilled up to 160°/20 mm.; the dark red residue, which gradually solidified, when recrystallised from benzene gave a further small yield of the dimethyldiquinolyl.

6 : 6′-*Dimethyl*-2 : 2′-*diquinolyl* crystallises from benzene in small, colourless needles, m. p. 202·5—203° (Found: C, 84·6; H, 5·8; *M*, in camphor by Rast's method, 279. $C_{20}H_{16}N_2$ requires C, 84·5; H, 5·6%; *M*, 284). It is moderately soluble in acetone, alcohol, or light petroleum and very soluble in chloroform. It is readily soluble in hot benzene or toluene, less soluble in the cold.

The *hydrochloride* crystallises from hot water in very minute needles. The *picrate*, obtained from the base and picric acid in alcoholic solution, is practically insoluble in acetone, benzene, or chloroform, but fairly soluble in glacial acetic acid, from which it crystallises in small, yellow needles, m. p. 282—283° (decomp.). The *ethiodide*, $C_{20}H_{16}N_2,C_2H_5I$, prepared by heating the base with excess of ethyl iodide in a sealed tube at 150° for 1½ hours, crystallised from much alcohol in sparkling needles, m. p. 277—278° (decomp.; darkening at 275°) (Found: I, 28·2. $C_{20}H_{16}N_2,C_2H_5I$ requires I, 28·9%).

7 : 7′-*Dimethyl*-2 : 2′-*diquinolyl* (II).—7-Methylquinoline (38 g.) and sodium (4 g.) were heated together, and the product was treated with ether, as described above. The brown residue was recrystallised several times from aqueous acetone to remove tarry impurities and finally from carbon tetrachloride. 7 : 7′-*Dimethyl*-2 : 2′-*diquinolyl* was thus obtained in tufts of colourless needles, m. p. 208—209° (Found: C, 84·0; H, 5·8%). It is soluble in alcohol, acetone, chloroform, ethyl acetate, or carbon tetrachloride, but crystallises best from the last-named.

The *picrate* crystallises from alcohol in slender, yellow needles, m. p. 285—286° (decomp.; darkening at 284°). The *ethiodide*, obtained by heating the base with ethyl iodide at 130° in a sealed tube for 1 hour, crystallises from alcohol in clusters of golden-yellow needles, m. p. 274—275° (decomp.).

8 : 8′-*Dimethyl*-2 : 2′-*diquinolyl* (III).—8-Methylquinoline (50 g.) and sodium (4 g.) were heated together under the conditions previously described, but little, if any, diquinolyl was formed; the heating was therefore continued at 150—160° during a further 24 hours. The very viscous, dark brown mass was treated as in the previous cases, the ether evaporated, and the oily product distilled up to 160°/20 mm. The residue, which set to a hard, resinous mass when cold, was dissolved in acetone, and water added until a turbidity ensued; in the course of 3 or 4 days, crystals embedded in resinous matter separated. These were freed from resin

by washing them with acetone, crystallised again from acetone, and fractionally crystallised from carbon tetrachloride (yield very poor).

8 : 8′-*Dimethyl*-2 : 2′-*diquinolyl* forms tufts of colourless needles, m. p. 147—147·5° (Found : C, 84·0; H, 5·6%; *M*, in camphor, 290). It is soluble in benzene, chloroform, alcohol, or ethyl acetate, and crystallises readily from ethyl bromide or ethyl iodide.

The *picrate*, precipitated on mixing alcoholic solutions of the base and picric acid, crystallises from ethyl acetate in yellow needles, m. p. 264—265° after darkening at 258°.

2-*Hydroxy*-6-*methylquinoline*.—When an intimate mixture of finely powdered, freshly fused potassium hydroxide (40 g.) and 6-methylquinoline (44 g.) was heated at 250°, hydrogen was evolved in the theoretical quantity. The cooled reaction mixture was dissolved in water, the solution filtered if necessary, and the crude methylcarbostyril precipitated by the addition of dilute hydrochloric acid. Recrystallised from hot water, it formed long, yellow needles, m. p. 225—230°, and therefore was still impure. On heating at 12 mm., it began to sublime at 50° and passed over at 240—241°; the colourless distillate crystallised from alcohol in monoclinic prisms, m. p. 232—233° (Einhorn and Lauch, *Annalen*, 1888, **243**, 359, give m. p. 228°) (Found : C, 75·6; H, 5·7. Calc., C, 75·5; H, 5·7%).

2-*Bromo*-6-*methylquinoline*.—6-Methylcarbostyril (14 g.) and phosphorus tribromide (30 c.c.) were heated together on the water-bath during 3 hours and the solution was then gently boiled during a further ½ hour. The liquid was poured into water and the 2-bromo-6-methylquinoline distilled in steam; it separated from the distillate in long, colourless needles (yield 5·3 g.) and from alcohol in long, faintly yellow needles, m. p. 117—118° (Fischer and Guthmann, *J. pr. Chem.*, 1916, **93**, 378, give m. p. 126°) (Found : Br, 36·2. Calc., Br, 36·0%).

The *picrate*, obtained from boiling alcoholic solution, crystallised from alcohol in glistening, golden needles, m. p. 140·5°. The *ethiodide*, $C_{10}H_8NBr,C_2H_5I$, prepared by heating the base with excess of ethyl iodide in a sealed tube at 130° during 1 hour, crystallised from ethyl acetate in yellow prisms, m. p. 110—111°.

Attempts to synthesise 6 : 6′-dimethyl-2 : 2′-diquinolyl from 2-bromo-6-methylquinoline by the Fittig-Wurtz reaction and by the use of Grignard reagents were unsuccessful.

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UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, June 24th*, 1925.]

CCLXXXIV.—*The Thermal Decomposition of Ozone.*

By Robert Owen Griffith and Andrew McKeown.

In an investigation of the reaction between ozone and hydrogen at 100°, the results of which will shortly be published, it was necessary to compare the intrinsic rate of the reaction $2O_3 \longrightarrow 3O_2$, which occurs simultaneously with the reaction $H_2 + O_3 \longrightarrow H_2O + O_2$, with the velocity of deozonisation in the absence of hydrogen. Several determinations of the rate of thermal decomposition of ozone have already been published, the most important being those of Warburg (*Ann. Physik*, 1902, **9**, 1286), Clement (*ibid.*, 1904, **14**, 342), Jahn (*Z. anorg. Chem.*, 1906, **48**, 260), Perman and Greaves (*Proc. Roy. Soc.*, 1908, *A*, **80**, 353), Chapman and Clarke (J., 1908, **93**, 1638), and Chapman and Jones (J., 1910, **97**, 2463). There is general agreement between these authors that the decomposition of ozone, allowed to proceed in clean glass vessels at temperatures up to 150°, is apparently of the second order, a much better bimolecular than unimolecular constant being obtained, and there is also agreement as regards the order of magnitude of the bimolecular velocity coefficient at a common temperature, *e.g.*, 100°. There is conflict of opinion, however, regarding (*a*) the nature of the reaction, whether it is essentially homogeneous or heterogeneous, (*b*) the effect of pressure on the reaction velocity, and (*c*) the effect of addition of inert gases such as nitrogen. Chapman and Clarke believe that the reaction is practically a homogeneous one, while Perman and Greaves consider that their results indicate the surface of the containing vessel to be the main seat of the change. The present work was not undertaken for the purpose of deciding this point experimentally; our attention has been mainly confined to the effect of addition of other gases and variation of the partial pressure of oxygen on the velocity.

Jahn (*loc. cit.*) found that the velocity of deozonisation in mixtures of ozone and oxygen is inversely proportional to the partial pressure of the latter gas, while Perman and Greaves also found an increased velocity on diminishing the pressure of oxygen, although the effect was less than that obtained by Jahn. On the other hand, Chapman and Jones state that variation in the partial pressure of oxygen in ozonised oxygen is unattended by appreciable change in the velocity of deozonisation. The latter investigators were also unable to detect any effect due to admixture with nitrogen, although this was found by Jahn and by Perman and Greaves to increase the rate of decomposition of ozone.

In view of these discrepancies and also as the results would be of interest for comparison with corresponding velocity data for this reaction in the presence of hydrogen, experiments on the rate of deozonisation at 100° in ozonised oxygen at various pressures and in mixtures of ozonised oxygen with helium, with argon, with nitrogen, and with carbon dioxide have been carried out.

Experimental.

The velocity of deozonisation was measured by the static method, the difference in pressure between the reaction tube and a compensator tube, containing air and maintained at the same temperature, being registered by a manometer containing concentrated sulphuric acid.

The apparatus and experimental methods employed were those of Griffith and Shutt and of Griffith and MacWillie (J., 1923, **123**, 2752, 2767) suitably modified; the materials used in this work are also described in the same papers.

All the experiments were carried out at approximately 100°.

The reaction was followed for 2 to 3 hours, after which the reaction and compensator tubes were quickly cooled to room temperature * and the residual ozone was determined analytically. From the amount of ozone thus found, one could calculate the pressure increase which has to be added to the last pressure difference obtained at 100° to give the value of p_∞, the pressure reading which would have been observed had the reaction gone to completion.

If θ_1 = room temperature,* θ_2 = temperature of the steam, p = pressure increase required (expressed in mm. H_2SO_4), v = common volume of reaction and compensator tubes in c.c., z = number of gram-molecules of residual ozone in reaction tube, π_{θ_1} = total pressure at the temperature θ_1 in the reaction tube expressed in mm. H_2SO_4, and γ = volume of the manometer tubing in c.c. per mm., then it may be shown that

$$p = z \times 380 \times 13{\cdot}59 \times 22412 \times (273 + \theta_1) \times R/(1{\cdot}84 \times 273 \times v \times \alpha).$$

Here $\alpha = (1 + \gamma\pi_{\theta_1})/v$ (compare Griffith and Shutt, *loc. cit.*, p. 2756) and R is a factor the value of which would have been equal to the ratio of the absolute temperatures $273 + \theta_2$ and $273 + \theta_1$, had there been no "dead" space at the higher temperature θ_2, and had there been no alteration in the effective volumes of the reaction and compensator tubes owing to the motion of the manometric liquid. The value of R was determined experimentally;

* In reality, the temperature of the town water supply. The value of ϑ_1 for each experiment is not given in the tables. The mean value for the experiments given in Tables III and IV was 8°.

it depends on the ratio of " dead " space to volume of reaction tube and also on the total pressure; the values found are given in the tables.

Values of the bimolecular velocity coefficients ($k_{obs.}$) were calculated from

$$k_{obs.} = \frac{1}{t_2 - t_1}\left\{\frac{1}{p_\infty - p_2} - \frac{1}{p_\infty - p_1}\right\},$$

p_1 and p_2 being the observed manometric differences at the temperature θ_2 at times t_1 and t_2, respectively (time in minutes).

The coefficients were calculated in all cases between successive time readings, this method being the one best suited to show the magnitude of any " trend " in the constants.

From the values of $k_{obs.}$, the absolute values (k_a) of the coefficients in the units litres/moles-minutes were calculated from the equation

$$k_a = k_{obs.} \times \frac{R}{\alpha} \times (273 + \theta_1) \times 380 \times \frac{13{\cdot}59}{1{\cdot}84} \times 0{\cdot}08207.$$

Four reaction tubes were employed.*

Tube A : of German glass, 42 cm. long and approximately 2 cm. in diameter; volume = 126·5 c.c.; containing 2·0 c.c. of concentrated sulphuric acid spread along its entire length.

Tube B : of German glass, 41 cm. long, 2 cm. in diameter; volume = 125·0 c.c.; containing 3·0 c.c. of concentrated sulphuric acid spread along its entire length.

Tube C : of glass of unknown origin, 31 cm. long, approximately 2·6 cm. in diameter; volume = 153·8 c.c.

Tube D : of English glass, length = 39 cm., diameter = 2·2 cm.; volume = 156·6 c.c.

Most of the experiments were carried out with tube D. Only a few experiments could be carried out with tube A before it cracked, while tube C, though apparently its inner surface was as carefully cleaned as that of the others, gave far higher velocity coefficients and probably contained a trace of some catalytic material. The results of the three experiments performed with this tube are included in the table of results for comparison.

The velocity of deozonisation was determined at 100° with ozonised oxygen under pressures of approximately 330, 540, 760 and 1000 mm. of mercury. Experiments were also carried out at the same temperature, employing mixtures in various proportions of ozonised oxygen with helium, with argon, with nitrogen

* A few preliminary experiments were carried out in a fifth tube. The results (not here presented) agreed well with those obtained with Tubes A, B, and D.

and with carbon dioxide. The total pressure in these cases was either 760 or 1000 mm.

The reaction does not follow a strictly bimolecular course, there being a tendency for the second-order coefficients to increase with time, *i.e.*, with diminishing concentration of ozone. This increase, however, is small in ozonised oxygen mixtures under the highest pressures employed, but becomes rather more marked when the total pressure is reduced. In the presence of excess of any one of the four diluent gases investigated and when the total pressure was 1000 mm. of mercury, no sensible rise in the coefficient with time was observed.

Tables I, II, III, and IV summarise the results. Tables I and II relate to preliminary experiments carried out employing tubes A, B, and C, Tables III and IV to the final series, all the experiments in which were obtained with the same reaction tube D. In these tables, P_{θ_2} = total initial pressure of reaction mixture in mm. of mercury at the temperature θ_2; $p^{0_2}_{\theta_2}$ = sum of initial partial pressures of oxygen and ozone, which may be taken as the mean partial pressure of oxygen during the experiment; and $p^{z}_{\theta_2}$ = partial pressure of the added gas. The values given under $k_{\text{obs.}}$ are the highest and lowest values obtained for this bimolecular coefficient; $k'''_{\text{obs.}}$ is the weighted mean value of $k_{\text{obs.}}$, k'''_a is the absolute value corresponding to $k'''_{\text{obs.}}$, and k'''_a (corr.) is this absolute value corrected to a uniform temperature of 100°, using the figure 2·5 obtained by Warburg (*loc. cit.*) for the temperature coefficient of the reaction. The assumption here made, that this temperature coefficient is independent of the total pressure and composition of the gas mixture, can lead to no serious error, since in no case does the temperature of observation deviate from 100° by more than 1·2°.

TABLE I.

Ozone–Oxygen Mixtures.

No. of expt.	Tube.	θ_2.	P_{θ_2}.	a.	R.	$k_{\text{obs.}} \times 10^4$.	$k'''_{\text{obs.}} \times 10^4$.	k'''_a.	k'''_a (corr.).
5	A	99·5	752	1·123	1·210	1·10—1·37	1·20	8·57	8·98
6	A	99·4	743	1·121	,,	1·15—1·45	1·28	9·14	9·67
7	A	99·7	750	1·123	,,	1·12—1·45	1·27	9·06	9·33
8	A	100·15	754	1·123	,,	1·15—1·45	1·34	9·60	9·47
9	A	99·9	757	1·124	,,	1·15—1·60	1·28	9·13	9·22
10	B	99·9	762	1·124	1·214	1·29—1·64	1·38	9·67	9·76
11	B	99·8	758	1·124	,,	1·20—1·56	1·34	9·39	9·57
13	B	100·2	768	1·125	,,	1·29—1·56	1·41	10·0	9·82
16	B	99·15	743	1·121	,,	1·18—1·47	1·29	9·12	9·88
20	B	100·0	1003	1·162	1·196	1·03—1·45	1·16	7·77	7·77
21	C	100·2	766	1·100	1·246	2·53—5·40	—	—	—
22	C	100·1	763	1·100	,,	2·18—3·86	—	—	—
23	C	100·2	775	1·101	,,	1·84—2·62	—	—	—

Table II.

Mixtures of Ozonised Oxygen with Helium, Argon, and Nitrogen.

No. of expt.	Tube.	Addition.	θ_2.	P_{θ_2}.	$p^{O_2}_{\theta_2}$.	$p^{x}_{\theta_2}$.	α.	R.	$k_{obs.}\times10^4$.	$k^m_{obs.}$ $\times10^4$.	k^m_a.	k^m_a (corr.)
14	B	Argon	100·15	768	461	307	1·125	1·214	2·10—2·70	2·25	15·9	15·7
17	B	,,	99·4	746	435	311	1·121	,,	1·75—2·30	1·99	14·2	15·0
15	B	Nitrogen	99·6	749	414	335	1·121	,,	2·06—2·68	2·33	16·5	17·1
18	B	Helium	99·8	755	440	315	1·123	,,	1·91—2·48	2·20	15·6	15·8
19	B	,,	100·2	767	447	320	1·124	,,	2·02—2·81	2·42	17·0	16·7

Table III.

Ozone–Oxygen Mixtures. Tube D.

No. of expt.	θ_2.	P_{θ_2}.	α.	R.	$k_{obs.}\times10^4$.	$k^m_{obs.}$ $\times10^4$.	k^m_a.	k^m_a (corr.).
41	99·7	335	1·044	1·288	1·84—2·61	1·90	15·1	15·6
47	99·8	335	1·044	,,	2·10—2·58	2·15	17·1	17·4
33	100·3	529	1·069	1·269	1·63—2·10	1·70	13·0	12·6
46	99·4	540	1·071	,,	1·46—2·03	1·51	11·5	12·2
34	100·0	559	1·073	,,	1·68—2·12	1·75	13·4	13·4
24	100·1	766	1·101	1·243	1·34—1·47	1·40	10·2	10·1
25	100·0	755	1·100	,,	1·30—1·62	1·37	10·0	10·0
26	99·9	759	1·100	,,	1·40—1·63	1·44	10·5	10·6
29	99·8	752	1·099	,,	1·42—1·75	1·50	10·9	11·1
36	99·9	753	1·099	,,	1·35—1·80	1·40	10·2	10·3
31	100·0	1015	1·133	1·220	1·15—1·38	1·20	8·33	8·33
32	100·2	1021	1·133	,,	1·22—1·37	1·23	8·52	8·37

Table IV.

Mixtures of Ozonised Oxygen with Helium, Argon, Nitrogen, and Carbon Dioxide. Tube D.

No. of expt.	Addition.	θ_2.	P_{θ_2}.	$p^{O_2}_{\theta_2}$.	$p^{x}_{\theta_2}$.	α.	R.	$k_{obs.}\times10^4$.	$k^m_{obs.}$ $\times10^4$.	k^m_a.	k^m_a (corr.).
39	Nitrogen	99·8	1003	334	669	1·133	1·220	3·32—3·68	3·46	24·1	24·6
44	Helium	99·0	976	325	651	1·128	,,	2·56—3·35	2·91	20·3	22·3
45	,,	99·0	974	325	649	1·128	,,	2·72—3·15	2·86	19·9	21·9
49	,,	99·8	1005	335	670	1·133	,,	2·87—3·18	3·00	20·8	21·2
42	Argon	99·4	993	331	662	1·132	,,	3·40—4·46	3·94	27·4	29·0
43	,,	99·3	984	328	656	1·130	,,	3·48—4·00	3·73	26·0	27·8
48	,,	99·9	1012	337	675	1·133	,,	3·90—4·40	4·11	28·5	28·8
40	CO_2	99·9	1004	335	669	1·133	,,	3·29—3·76	3·48	24·2	24·4
37	Nitrogen	100·2	1016	762	254	1·133	1·220	1·57—1·91	1·65	11·4	11·2
38	Helium	100·3	1026	770	256	1·134	,,	1·51—2·27	1·57	10·9	10·6
27	Helium	99·7	751	441	310	1·100	1·243	2·17—2·45	2·30	16·8	17·3
28	Nitrogen	99·7	750	456	294	1·100	,,	2·01—2·63	2·15	15·8	16·2
35	CO_2	99·6	754	440	314	1·100	,,	2·22—2·53	2·35	17·7	17·7
30	Nitrogen	100·3	766	519	247	1·101	1·243	2·10—2·62	2·20	16·0	15·5

The velocity of deozonisation in ozonised oxygen obtained with tube C (Table I, experiments 21—23) is much higher than that found employing any of the other tubes with the reaction mixture

at the same total pressure of 760 mm.; also the relative increase in the coefficient as the reaction proceeds is greater. Experiments 21—23 were carried out in the order given and it is of interest to note that the catalytic material of unknown nature present on the surface of the tube was gradually being rendered less active, as evidenced by the progressive fall in the velocity coefficients; possibly, had work with this tube been continued, the constant $k_{obs.}$ would eventually have fallen to the value obtaining in the other tubes. In connexion with this change of catalytic activity of the surface of the reaction vessel, a somewhat analogous effect was observed with tube D. After the experiments given in Tables III and IV had been completed, a fresh series carried out in the same tube (D) gave uniformly smaller coefficients than those recorded in Tables III and IV. Table V summarises a few of these experiments. The constants are now of the order of 10% less than those previously obtained under analogous conditions.

TABLE V.

Tube D.

No. of expt.	Addition.	θ_2.	P_{θ_2}.	$p^{O_2}_{\theta_2}$.	$p^{x}_{\theta_2}$.	a.	R.	$k_{obs.}\times10^4$.	$k_{obs.}$ $\times10^4$.	k^m_a.	k^m_a (corr.).
54	—	98·85	758	758	—	1·100	1·243	1·08—1·28	1·12	8·11	9·04
55	—	100·5	1029	1029	—	1·134	1·220	1·11—1·21	1·16	8·03	7·66
56	—	100·3	335	335	—	1·104	1·288	1·78—2·52	1·98	15·7	15·2
50	Argon	99·35	993	745	248	1·130	1·220	1·52—1·80	1·54	10·7	11·4
51	Nitrogen	99·0	984	738	246	1·129	,,	1·24—1·53	1·32	9·16	10·1
52	Helium	99·0	976	734	245	1·129	,,	1·21—1·57	1·27	8·85	9·75
58	Argon	99·8	1006	405	601	1·132	1·220	2·96—3·90	3·11	21·6	22·0
57	Helium	100·0	1015	409	606	1·133	,,	2·24—2·89	2·44	17·0	17·0

The coefficients obtained with tubes A and B containing sulphuric acid (Tables I and II) are only slightly lower than those obtained under identical conditions of pressure and composition of gas mixture in tube D, which contained no sulphuric acid (Tables III and IV). Since the catalytic effect of the glass surfaces of tubes A and B might have differed from that of D, a few experiments were carried out with tube D to test the effect of addition of sulphuric acid. The velocity coefficient was first determined for ozonised oxygen at a pressure of 755 mm., 3·9 c.c. of concentrated sulphuric acid were introduced into the tube so that it spread over its whole length (approximately one-eighth of the inner surface was covered by the acid), and the velocity coefficient was redetermined with the following results :—

Expts. 59 and 62 : No H_2SO_4 present; k^m_a (corr.) $= \left.\begin{matrix}9\cdot71\\9\cdot87\end{matrix}\right\}9\cdot79.$

Expts. 63 and 64 : In presence of H_2SO_4; k^m_a (corr.) $= \left.\begin{matrix}9\cdot31\\9\cdot45\end{matrix}\right\}9\cdot38.$

A slight diminution in the value of the velocity coefficient is therefore caused when part of the glass surface is replaced by one of sulphuric acid.

Discussion of Results.

Tables III and IV contain the main results of this work and summarise a number of determinations of the velocity of deozonisation at 100° under various conditions. These data were obtained with the same reaction tube D, and with (it is believed) its surface in a constant condition as regards possible catalytic action.

The tables show that :—

(*a*) The velocity of deozonisation in mixtures containing only ozone and oxygen is a function of the oxygen pressure, as already found by Jahn and by Perman and Greaves, but later contradicted by Chapman and Jones. We find that the velocity coefficient increases with decreasing total pressure, but the two quantities are not inversely proportional as stated by Jahn, rather their product diminishes as the pressure decreases. Actually it is found that the variation of k_a^m with pressure in tube D is very closely reproduced by the empirical relation $k_a^m = 11{,}500/(360 + P_{\theta_2})$.

The absolute values of the bimolecular velocity coefficient found by us are in fair agreement with those obtained by Warburg and by Perman and Greaves at the same temperature and under corresponding conditions of pressure. Thus, for ozonised oxygen at 100° and a pressure of 1000 mm. of mercury, we find $k_a^m = 7{\cdot}77$ for tube B and 8·35 for tube D, while Warburg gives a mean value, $k_a^m = 7{\cdot}54$. At 100° and 758 mm. pressure, our value of k_a^m (tube D) = 10·3 agrees fairly closely with that calculated from the results given by Perman and Greaves (Globe II), *viz.*, 9·72.

(*b*) The addition of any one of the gases nitrogen, argon, helium, and carbon dioxide causes an increase in the velocity of deozonisation, if the reaction velocity in the presence of one of these gases is compared with that found in ozonised oxygen alone with the same partial pressure of oxygen. In virtue of (*a*), this increase is still more pronounced if the coefficient found in the presence of one of these gases is compared with that observed in ozonised oxygen under the same *total* pressure. This increase in velocity is very marked when the partial pressure of the added gas is large. Thus the velocity coefficient k_a^m for ozonised oxygen at a pressure of 335 mm. is about 16·5 (mean of the results of experiments 41 and 47), whilst, in a mixture containing oxygen at the same partial pressure, but with a partial pressure of argon of 660 mm., the constant is now 28·5 (experiments 42, 43, and 48).

The increased velocity of deozonisation caused by addition of nitrogen is in qualitative agreement with the results of Jahn at

the higher temperature 127°, and of Perman and Greaves at 100°. Quantitatively, however, the relative increase in the coefficient observed by the latter investigators is somewhat greater than that obtained in the present work with the same gas mixture. On the other hand, Chapman and Jones could not detect any increase in the rate of reaction resulting from displacement of part of the oxygen in ozonised oxygen by nitrogen.

(*c*) The positive catalytic effects of the four gases investigated are in the order argon greatest, followed by nitrogen and carbon dioxide with approximately equal effects, and helium least. This order bears no relation to the catalytic effects found for these gases by Griffith and MacWillie on the rate of photochemical decomposition of ozone by visible light.

A necessary preliminary to any attempt at an explanation of the results presented in this paper appears to involve an answer to the question as to whether the decomposition of ozone under the conditions here investigated occurs mainly in the homogeneous gaseous phase or at the glass surface of the containing vessel. We are unable from the results of the present work or from the results of previous workers to arrive at a definite conclusion on this point. All that may safely be inferred is that some part at least of the measured rate is due to a heterogeneous change. This is shown by the slight variation in the velocity coefficient from tube to tube and by the retarding effect produced by covering a portion of the glass surface by sulphuric acid. We believe that our results may best be interpreted in the following way. The main reaction is a homogeneous change and is accompanied by a heterogeneous reaction whose velocity involves a lower power of the ozone concentration. This would explain the increase in the value of the bimolecular coefficient in each experiment with time, and in particular the relatively greater increase of this function with time the lower the pressure, *i.e.*, the lower the initial concentration of ozone. The few experiments carried out with tube C (21—23, Table I) support this view. Here apparently we are dealing with a case where the catalytic activity of the surface, and therefore the rate of the heterogeneous reaction, is of far greater significance than in the experiments with the other tubes. It will be observed that in these three cases, the greater the velocity of deozonisation, the greater also is the relative increase in the calculated bimolecular coefficient with time. This result is consistent with the conception of a constant intrinsic rate for the homogeneous process, together with a gradually decreasing catalytic activity of the surface which governs the intrinsic rate of the heterogeneous process.

If the observed reaction is a mixture of homogeneous and heterogeneous changes, which of these is it that the inert gases catalyse? Presumably, it is not the rate of heterogeneous change which is affected, and this for two reasons: (1) the velocity coefficient varies less with time in the presence of an inert gas than in its absence, indicating that the homogeneous change is accelerated relative to the heterogeneous change of lower order; (2) not only is the power of adsorption of such gases as argon and helium by glass surfaces small, but it is difficult to see how such adsorption could produce any other than a retarding effect on a heterogeneous change. We must therefore conclude that the catalytic effect of the inert gases investigated takes place in the gaseous phase.

We have thus to explain the retardation of the velocity of the homogeneous reaction by increase of the pressure of oxygen, and its acceleration by introduction of an inert gas. The effect of oxygen has been interpreted by Jahn (*loc. cit.*) in terms of the reaction scheme: $O_3 \rightleftharpoons O_2 + O$; $O + O_3 \longrightarrow 2O_2$, leading to $k_{obs.} \propto [O_3]^2/[O_2]$. This relation, however, is not in agreement with our experimental results; further, it appears improbable that the energy relations of the process of deozonisation are consistent with the formation of oxygen atoms at a temperature of 100°. If this mechanism be discarded, there remain such possibilities as:

(1) $O_3 \rightleftharpoons O_3^*$; $O_3^* + O_3 \longrightarrow 3O_2$,

where O_3^* represents an activated ozone molecule; or

(2) $O_3 \rightleftharpoons O_3^*$; $O_3^* + O_3 \rightleftharpoons$ complex; complex $\longrightarrow 3O_2$.

A qualitative agreement with the results of the present work may be obtained on the basis of this second possibility, if we make the following assumptions:

(*a*) The complex may either revert spontaneously into ozone molecules or decompose into oxygen molecules.

(*b*) Either of these changes may also be brought about by collision of the complex with an indifferent molecule.

Depending upon the type of the colliding molecule, one of these "decomposition by collision" processes will be favoured at the expense of the other. In this sense our results indicate that collisions with oxygen molecules favour the reversal: complex $\longrightarrow 2O_2$, whereas it is the process: complex $\longrightarrow 3O_2$ which is assisted by collision with inert gas molecules in the order argon, nitrogen, carbon dioxide, helium.

In connexion with the above assumptions, some theoretical considerations regarding the mechanism of chemical reactions which have recently been advanced by Christiansen (*Z. physikal. Chem.*, 1924, **113**, 35) and by Born and Franck (*Z. Physik*, 1925, **31**, 411) are of interest. Christiansen considers the first stage in

a bimolecular reaction to be the formation by collision of an active complex. This complex can subsequently decompose spontaneously into resultants, or can suffer deactivation by collision with a third molecule. Accordingly the probability that reaction should take place is determined by a factor of the form $\rho/(\rho + \Sigma\eta C)$, where ρ denotes the probability of spontaneous reaction, C is the concentration of any molecular species present, and the η's are specific coefficients such that $\Sigma\eta C$ gives the probability of deactivation of the complex by collision. Born and Franck have also dealt with deactivation processes occurring in chemical reactions, but from a somewhat different point of view. They conclude that, in order that additive processes of the type $A + B \longrightarrow AB$ may occur, it is necessary that the activated complex (or quasi-molecule) AB* first formed should, during its life period, suffer collision with a third molecule, whose function is to remove the difference in energy between AB* and AB. [On the other hand, they consider that, for substitution processes as $A + B \rightarrow C + D$ to occur, such ternary collisions are unnecessary.] Accordingly, the reaction velocity coefficient of Born and Franck should contain a function of the type $\Sigma\eta_1 C/(\rho_1 + \Sigma\eta_1 C)$, a function which is in a sense complementary to that of Christiansen; ρ_1, however, now defines the intrinsic probability of the reversal $AB^* \longrightarrow A + B$, and the η_1's refer to the change $AB^* \longrightarrow AB$.

The suggestions made by us in the reaction mechanism for the process of deozonisation include all four of the possibilities of change on the part of the complex entertained by Christiansen and Born and Franck. As a result, our final expression for the bimolecular velocity coefficient would contain a complex probability term of the form $(\rho + \Sigma\eta C)/(\rho + \rho_1 + \Sigma\eta C + \Sigma\eta_1 C)$ in which ρ and η refer to the change : complex $\longrightarrow 3O_2$ and ρ_1 and η_1 to the change : complex $\longrightarrow 2O_3$. As already stated, these possibilities afford a qualitative explanation of our results.

While it is not suggested that the mechanism postulated is necessarily the correct one, we believe that an explanation of the "negative" catalytic effect of oxygen and the "positive" effect of the other gases must involve considerations of the nature indicated above.

Summary.

The velocity of the thermal reaction $2O_3 \longrightarrow 3O_2$ has been determined at 100° in glass tubes in the presence and absence of sulphuric acid. The reaction follows approximately a bimolecular course, the velocity coefficients increasing slightly, however, with time. For ozonised oxygen mixtures, at pressures between 300 mm. and 1000 mm., the bimolecular coefficient k (expressed in the

units litres/moles-minutes) is given by $k = 11{,}500/(360 + P)$, where P = the pressure in mm. of gas mixture.

For mixtures of ozonised oxygen with any one of the gases argon, nitrogen, carbon dioxide, and helium, the velocity of deozonisation is greater than that found for ozonised oxygen with the same partial pressure of oxygen. This positive "catalytic" effect, which is greatest for argon and least for helium, increases with increasing partial pressure of added gas.

A short discussion of these results and of a possible mechanism of the reaction process is given.

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CCLXXXV.—*The Dissociation Pressures of Hydrated Double Selenates.*

By JOHN FERGUSON.

IN two former papers (J., 1922, **121**, 1407; 1924, **125**, 1307) the author in conjunction with R. M. Caven communicated an account of the dissociation pressures of hydrated double sulphates of the type $M''SO_4,M'_2SO_4,6H_2O$. The present paper contains the results of measurements of the dissociation pressures of hydrated double selenates of the same type.

The apparatus and methods employed have already been described (*loc. cit.*).

Each double selenate was prepared by crystallisation from a solution containing the two simple selenates in equivalent proportions. Selenium was the starting point in the preparation of the simple selenates. It was converted into copper selenate by Dennis and Koller's method (*J. Amer. Chem. Soc.*, 1919, **41**, 949), and this salt was electrolysed in warm saturated solution (Metzner, *Compt. rend.*, 1898, **127**, 54), yielding selenic acid, from which the simple selenates were obtained by neutralisation with the corresponding carbonates or hydroxides. The double selenates were analysed to test their purity.

The double selenates examined yielded dihydrates as the first stage in their dehydration. Induction lag phenomena were hardly so marked as in the case of the sulphates (J., 1924, **125**, 1308).

The pressures observed are equilibrium pressures in systems of the type $M''SeO_4,M'_2SeO_4,6H_2O \rightleftharpoons M''SeO_4,M'_2SeO_4,2H_2O+4H_2O$.

Copper Potassium Selenate.

Temp.	25·1°	32·5°	39·1°	45·1°	50·7°	61·7°	50·0°	42·7°	36·2°
Press.	11·8	21·7	36·4	55·3	79·9	137·2	77·7	48·3	28·7

Copper Rubidium Selenate.

Temp.	24·9°	32·3°	41·1°	49·6°	59·1°	58·3°	74·8°	67·1°	51·9°	34·4°
Press.	8·0	13·5	24·4	42·4	77·9	73·7	192·0	121·0	49·3	16·2

Copper Cæsium Selenate.

Temp.	27·7°	36·0°	42·7°	50·0°	56·2°	59·2°	65·2°	61·2°	51·2°	32·3°
Press.	22·8	37·9	54·7	81·1	110·5	125·9	164·5	139·1	86·6	48·7

Copper Ammonium Selenate.

Temp.	25·0°	30·6°	35·3°	40·0°	50·8°	60·3°	70·4°	57·3°	44·9°	27·7°
Press.	2·8	5·5	7·5	10·6	26·3	48·5	90·8	38·9	16·2	4·1

Copper Thallous Selenate.

Temp.	29·9°	40·0°	48·0°	53·9°	64·1°	59·2°	44·5°	35· °
Press.	8·9	20·3	36·3	53·6	99·6	75·0	28·7	13·3

Cobalt Potassium Selenate.

Temp.	26·1°	33·0°	42·5°	48·5°	61·2°	68·2°	43·8°	28·4°
Press.	21·4	33·5	58·5	79·9	148·5	199·2	62·4	26·8

Cobalt Ammonium Selenate.

Temp.	27·0°	34·1°	41·5°	56·3°	65·6°	68·4°	71·1°
Press.	3·4	5·9	10·3	29·7	53·1	64·8	75·5

Zinc Potassium Selenate.

Temp.	31·3°	42·6°	48·5°	57·2°	71·3°	59·9°	37·2°
Press.	23·6	50·7	75·4	120·3	218·3	136·2	36·2

Zinc Ammonium Selenate.

Temp.	31·3°	42·6°	48·5°	57·2°	71·3°	59·9°	37·2°
Press.	2·9	6·9	10·1	19·9	46·5	22·8	4·1

Nickel Potassium Selenate.

Temp.	29·9°	40·0°	48·0°	53·9°	64·1°	59·2°	35·1°
Press.	11·9	25·3	44·4	63·9	119·0	88·7	18·3

Nickel Rubidium Selenate.

Temp.	30·2°	38·2°	52·3°	62·0°	75·9°	54·2°	45·0°
Press.	1·5	3·1	9·0	16·0	37·9	9·9	5·3

Nickel Cæsium Selenate.

Temp.	30·2°	38·2°	52·3°	62·0°	75·9°	54·2°	45·0°
Press.	15·8	26·8	59·4	95·9	157·4	64·8	39·8

Nickel Ammonium Selenate.

Temp.	28·3°	37·2°	43·6°	56·0°	63·2°	69·0°	77·0°	35·6°
Press.	1·0	2·0	3·2	8·2	13·9	20·3	32·2	1·7

Nickel Ammonium Chromate.

This salt was prepared by Brigg's method (J., 1903, **83**, 392). It effloresces slowly in air, forming a brown substance which has the composition of the anhydrous salt. The dissociation pressures of a mixture of the hexahydrated salt and this substance were measured.

Temp.	28·2°	34·8°	40·8°	45·3°	50·7°	56·0°	69·0°	76·7°	57·4°	27·7°
Press.	23·8	34·8	49·4	64·4	84·7	111·7	201·7	278·0	118·8	22·8

Clark and Buckner (*J. Amer. Chem. Soc.*, 1922, **44**, 242) and Clark (*Amer. J. Sci.*, 1924, **7**, 1) have carried out a long series of measurements of the stabilities of ammines of inorganic salts, as indicated by the temperatures at which the dissociation pressures of the ammines rise to a definite value (100 or 760 mm.). They have found that the stability *increases* with *diminishing* atomic volume of the positive part of the molecule, *e.g.*, in the series Cs, Rb, K, Na; Cd, Zn, Mn, Cu, Fe, and *increases* with *increasing* volume of the negative part, *e.g.*, in the series Cl, Br, I; MoO_4, CrO_4, SO_4, SeO_4. These results agree also with the work of Ephraim on the metallic ammines (*Ber.*, 1912, **45**, 1322).

In the following table are given the molecular volumes (determined by Tutton) of both double sulphates and selenates, and also the absolute temperatures at which their dissociation pressures attain a definite value (50 mm.).

Univalent metal or group.	Bivalent metal.	Sulphates.		Selenates.	
		T_{50}.	M.V.	T_{50}.	M.V.
Potassium	Copper	320·8°	197·8	316·6°	211·3
	Cobalt	325·9	197·1	312·5	208·6
	Zinc	327·8	196·2	315·2	208·8
	Nickel	336·8	195·3	323·9	206·1
Rubidium	Cadmium	313·5	216·4	—	—
	Manganese	315·2	213·7	—	—
	Copper	326·0	207·7	325·0	221·5
	Cobalt	335·0	206·5	—	—
	Zinc	339·0	205·6	—	—
	Nickel	346·3	204·8	354·0	217·0
Cæsium	Cadmium	315·0	229·3	—	—
	Manganese	319·9	226·4	—	—
	Copper	332·5	220·3	314·1	235·5
	Cobalt	334·0	219·7	—	—
	Zinc	336·8	218·0	—	—
	Nickel	345·0	217·4	322·8	229·2
Ammonium	Cadmium	317·3	217·5	—	—
	Manganese	317·2	215·5	—	—
	Copper	332·0	207·7	333·7	222·2
	Cobalt	336·8	208·0	337·2	218·1
	Zinc	341·4	206·4	345·0	217·7
	Nickel	354·0	205·5	358·0	216·5

In the case of double salts formed by the same univalent metal or group with different bivalent metals, the temperature at which a pressure of 50 mm. is attained increases with decreasing molecular volume. The constitution of these double salts is probably of the type $M'_2[M''(SeO_4)_2]$, since it is known that in solutions of some of them at least, the bivalent metal migrates partially to the anode during electrolysis. Hence it may be said that stability in the sulphate or selenate groups, taken separately, is favoured by diminishing molecular volume of the anion or negative part of the molecule.

However, it must be pointed out that, although the double selenates have always a much greater molecular volume than the corresponding sulphates, the rubidium and ammonium double selenates are more stable than the rubidium and ammonium double sulphates. The potassium and cæsium double selenates are less stable than the corresponding sulphates.

Nickel ammonium chromate cannot be strictly compared with the sulphate and selenate double salts, as it does not form a dihydrate, like the other two. It is, however, the least stable of the three nickel ammonium salts, and has probably a much greater molecular volume (Tutton, *Min. Mag.*, 1912, **16**, 169).

As regards the positive part of the molecule, it is found that, the bivalent metal being the same, the stability increases with increasing molecular volume of the salt, in the order K, Rb, NH_4. The cæsium salts are anomalous, because, although they have as a class the greatest molecular volume, they are intermediate in stability between the potassium and rubidium salts. This rule, however, does not apply to the cæsium double sulphates of copper, cadmium and manganese, which are more stable than the corresponding potassium and rubidium salts. In the case of the two double selenate groups examined (copper and nickel) the cæsium and potassium dissociation pressure–temperature curves intersect, the cæsium salts being the less stable at lower temperatures.

If the cæsium salts are excluded from consideration, it follows that stability in the series of hydrated double sulphates and selenates is favoured by increasing atomic or molecular volume of the kation or positive part of the molecule.

To sum up, while it is obvious that the specific influence of the various atoms and groups enters as a complicating factor, the results tend to show that the stabilities of the hydrated salts are closely connected with the atomic or molecular volumes of the atoms and groups composing their molecules. The stabilities appear to *increase* with *decreasing* molecular volume of the anion, but increase with *increasing* atomic or molecular volume of the kation.

This relation is opposite to that which obtains with the metallic ammines (Clark and Buckner, *loc. cit.*).

Summary.

1. The dissociation pressures of certain double selenates of the type $M'_2SeO_4,M''SeO_4,6H_2O$ in contact with the corresponding dihydrates have been measured over a range of temperature.

2. The stabilities of these salts, and also of the double sulphates, as measured by the absolute temperatures at which their dissociation pressures attain the value of 50 mm., are greatly influenced by the molecular and atomic volumes of the groups and atoms in the molecule.

3. The specific action of the different atoms and groups introduces irregularities, especially noticeable in the case of cæsium double salts, but in general the stabilities of the hydrates increase with increasing volume of the kation and decrease with increasing volume of the anion.

4. These two relationships are the inverse of those obtaining with the metallic ammines.

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CCLXXXVI.—*Researches on Chromammines. Part II. Hydroxopentamminochromic Salts and Electrical Conductivities of Chromammines.*

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A. *Hydroxopentammino-chromic(-cobaltic) Hydroxide.*

IT was shown in Part I (King, J., 1924, **125**, 1329) that the alkaline solutions obtained by treating chloropentamminochromic or aquopentamminochromic chloride with moist silver oxide, which had until then been regarded as solutions of aquopentamminochromic hydroxide, gave hydroxopentamminochromic picrate with excess of picric acid. (That this is not due to instability of the aquopentamminochromic salt has now been shown by preparing the latter from the nitrate.) Hence the solutions were considered

to contain not aquo– but hydroxo–pentamminochromic hydroxide, a view supported by their intense reddish-violet colour, which is characteristic of " purpureo " rather than " roseo " solutions.

Further investigation showed that the aquopentamminochromic salt was obtained with oxalic acid, which thus behaved similarly to mineral acids (Christensen, *J. pr. Chem.*, 1881, **23**, 26).

$2[Cr(NH_3)_5OH](OH)_2+3H_2C_2O_4=[Cr(NH_3)_5H_2O]_2(C_2O_4)_3+4H_2O$.

2 : 4-Dinitrophenol, a much weaker acid than picric acid, gave the aquo-salt with both the chrommamine and the cobaltammine alkaline solutions. Also picric acid gave the aquo-salt with the cobaltammine solution, though 2 : 4-dinitro-α-naphthol-7-sulphonic acid, a much stronger acid, gave the hydroxo-salt (Part I). In view of these anomalous results, the nature of the alkaline solutions has been investigated from the point of view of electrical conductivity. From measurements of the conductivities of their salts, the conductivities of the aquopentamminochromic and hydroxopentamminochromic ions at zero concentration were found to be 174·3 and 73·3 mhos at 0°, giving 489·3 and 283·3 mhos for the limiting conductivities of the hydroxides. The value obtained by extrapolation of the conductivity data for the chromammine alkaline solution was 283·9, completely confirming the view that it contained only hydroxopentamminochromic hydroxide. The data of Lamb and Yngve (*J. Amer. Chem. Soc.*, 1921, **43**, 2352) for the conductivity of " aquopentamminocobaltic hydroxide " at 0° (ignoring the figure for $c = 0{\cdot}0002683$) give on extrapolation ($n = 1{\cdot}30$) the value 296 at infinite dilution, in fair agreement with the value 287 required for hydroxopentamminocobaltic hydroxide.

Aquopentamminochromic picrate was precipitated, on mixing solutions of aquopentamminochromic nitrate and 200% excess of sodium picrate, as aggregates of golden-yellow needles (Found : Cr, 6·0; NH_3, 9·9; N, 22·9; H_2O, 3·3.

$$[Cr(NH_3)_5H_2O]\{C_6H_2O_7N_3\}_3,\tfrac{1}{2}H_2O$$

requires Cr, 6·1; NH_3, 10·0; N, 23·1; H_2O, 3·2%). The salt lost all its water and also 43% of its ammonia on heating at 100° for 3 hours, so this is not a suitable method for introducing the picrato-group into the complex.

Aquopentamminochromic oxalate was obtained on mixing solutions of hydroxopentamminochromic hydroxide (Christensen, *loc. cit.*) and oxalic acid (3 mols.), precipitation occurring on shaking and cooling. It was washed with a little water, and with alcohol until free from oxalic acid. The air-dried product consisted of irregular, orange plates (Found : Cr, 16·3; NH_3, 26·4; H_2O of crystallisation, 10·9. $Cr(NH_3)_5H_2O]_2(C_2O_4)_3,4H_2O$ requires Cr, 16·1; NH_3, 26·4; H_2O of crystallisation, 11·2%). After a week in a vacuum over phosphoric

oxide, the water of crystallisation was completely removed, together with 4% of the ammonia. The salt lost 47% of its ammonia on heating at 100° for 3 hours, but still retained more than half of the co-ordinated water. Thus it was not possible to prepare an oxalato-salt from it by heating.

Aquopentammino-chromic (*-cobaltic*) 2 : 4-*Dinitrophenoxide*.—Finely powdered 2 : 4-dinitrophenol (2 mols.) was shaken mechanically for an hour with a solution of hydroxopentammino-chromic (-cobaltic) hydroxide, when the pure aquopentammino-salt was obtained, the excess of hydroxide remaining uncombined. The sparingly soluble product was washed with water, then triturated and washed with methyl alcohol, leaving a bright yellow powder. Ammonia was estimated as for picrates (Morgan and King, J., 1922, **121**, 1723). A. (Found: Cr, 7·4; NH_3, 11·7; N, 21·3; H_2O, 5·2.

$$[Cr(NH_3)_5H_2O]\{C_6H_3O_5N_2\}_3,H_2O$$

requires Cr, 7·2; NH_3, 11·8; N, 21·2; H_2O, 5·0%). 66% of the ammonia was removed in 3 hours at 85°, together with all the water. B. (Found: Co, 7·7; NH_3, 11·0; N, 20·1; H_2O, 9·2. $[Co(NH_3)_5H_2O]\{C_6H_3O_5N_2\}_3,3H_2O$ requires Co, 7·7; NH_3, 11·1; N, 20·1; H_2O, 9·4%). The compound charred at 100°.

Interaction of Hydroxopentamminocobaltic Hydroxide and Picric Acid Solutions.—Using three mols. of picric acid, the pure aquopentamminocobaltic salt was precipitated (Morgan and King, *loc. cit.*) (Found: Co, 7·1; NH_3, 10·1. Calc., Co, 7·0; NH_3, 10·1%). Two mols. of picric acid gave a mixture of the aquo- and hydroxo-salts.

B. *Hydroxopentamminochromic Salts.*

The only salts of this series hitherto described are the dithionate (Jörgensen, *J. pr. Chem.*, 1882, **25**, 419; Dubsky, *ibid.*, 1914, **90**, 99), picrate and dipicrylamide (Part I). The sulphate, nitrate, chloride, bromide, iodide, chromate and oxalate have now been obtained. They are rose-red salts, much more soluble in water than the corresponding cobaltammines (Werner, *Ber.*, 1907, **40**, 4098). They give solutions only very slightly alkaline to litmus and do not liberate ammonia from ammonium salts in the cold. Thus the tendency to form aquo-salts is less pronounced than in the case of hydroxopentamminocobaltic salts. The co-ordinated hydroxyl group cannot be acetylated or carbonated. Unlike the hydroxopentamminocobaltic salts, they smell of ammonia and are unstable even in the dark. They can, however, be kept indefinitely in an ammoniacal atmosphere. The salts most readily obtained pure and in quantity are the sulphate and nitrate.

That these are not basic aquo- but hydroxo-salts is demonstrated as follows.

(*a*) The sulphate and chromate were obtained anhydrous, whilst the nitrate, bromide, and iodide contained less water than is required for an aquo-salt.

(*b*) Hydroxopentamminochromic picrate was obtained from the sulphate by double decomposition.

(*c*) The electrical conductivities at 25° and a dilution of 1024 litres were of the order required (234 to 268 mhos) for salts with two univalent ions outside the complex, by Werner's empirical rule (Werner and Miolati, *Z. physikal. Chem.*, 1894, **14**, 506). The values obtained for the sulphate, nitrate, chloride, and oxalate were 234·0, 260·8, 274·6 and 235·5. (The value 266·2 obtained for hydroxopentamminocobaltic nitrate also agrees with the rule.)

Hydroxopentamminochromic sulphate was obtained by adding the hydroxopentamminochromic hydroxide solution (100 c.c.) from 4 g. of chloropentamminochromic chloride to 2·17 g. of ammonium sulphate in 3 c.c. of water and 16 c.c. of concentrated ammonia solution. When 50 c.c. of ice-cold alcohol had been added drop by drop to the cooled solution, rosettes of large, rose-red needles began to form. On addition of 20 c.c. more alcohol most of the sulphate crystallised (3·5 g.). It was collected, washed with ammoniacal alcohol and ether, and kept in a vacuum in presence of soda-lime and ammonium carbonate (Found : Cr, 21·2; NH_3, 33·8; S, 13·0. $[Cr(NH_3)_5OH]SO_4$ requires Cr, 20·8; NH_3, 34·0; S, 12·8%).

A sample was triturated with acetic anhydride for 20 minutes. The product was dissolved in water and treated with a solution of sodium picrate. Hydroxopentamminochromic picrate (Part I) was precipitated, showing that no acetylation had occurred (Found : Cr, 8·3; NH_3, 12·8; N, 23·3. Calc., Cr, 7·9; NH_3, 13·0; N, 23·5%).

When carbon dioxide was passed into a cooled concentrated solution of the sulphate, 3 to 4 mols. of ammonia were displaced, an insoluble bluish-violet carbonate of variable composition being formed.

Hydroxopentamminochromic nitrate was not readily obtained by adding the hydroxide to ammonium nitrate solution, as a large excess of alcohol and ether was needed for precipitation and the salt then separated as an oil. Five g. of aquopentamminochromic nitrate (Werner and Surber, *Annalen*, 1914, **405**, 220) were dissolved in 30 c.c. of concentrated ammonia, and cooled alcohol (60 c.c.) was added drop by drop to the ice-cold solution until a permanent crystalline precipitate formed (small, irregular, red plates). This was collected immediately and washed with ammoniacal alcohol and ether (Found: Cr, 18·2; NH_3, 29·6; N, 34·3.

$$[Cr(NH_3)_5OH](NO_3)_2,\tfrac{1}{2}H_2O$$

requires Cr, 18·1; NH_3, 29·7; N, 34·1%). Although the salt had

an ammoniacal odour, it lost only 2½% of its ammonia when kept during 10 weeks over phosphoric oxide in a vacuum.

Action of Pyridine on Aquopentamminochromic Nitrate.—A strong solution of the aquo-salt was treated with excess of ice-cold pyridine, the colour changing from orange to dark red. Addition of alcohol gave an orange precipitate, the ammonia content of which (26·1%) indicated that 25% of the aquo- had been hydrolysed to the hydroxo-nitrate.

Aquopentamminochromic halides, prepared by Christensen (*loc. cit.*) from hydroxopentamminochromic hydroxide, were more conveniently obtained in pure condition as follows.

Chloride.—A solution of 7·5 g. of aquopentamminochromic nitrate in 60 c.c. of water was filtered into 160 c.c. of ice-cold strong hydrochloric acid, when partial precipitation of the crystalline salt occurred. Ice-cold alcohol (100 c.c.) was added and the salt was at once collected (3·7 g.) (Found : NH_3, 32·7. Calc., NH_3, 32·6%). The chlorine was completely and immediately precipitated in the cold by silver nitrate, showing that no chloropentamminochromic salt was present.

Bromide.—A solution of 5 g. of aquopentamminochromic nitrate was added to 60 c.c. of ice-cold strong hydrobromic acid, an immediate precipitate of 5 g. of the bromide being formed. This was freed from a trace of purpureo-salt by dissolving in water (50 c.c.) and filtering into 50 c.c. of ice-cold hydrobromic acid. The *iodide* was prepared similarly to the bromide.

Hydroxopentamminochromic chloride was obtained as aggregates of small, very soluble, rose needles (2 g.) on dissolving aquopentamminochromic chloride (3 g.) in 15 c.c. of concentrated ammonia and slowly adding ice-cold alcohol (60 c.c.) until precipitation was complete. The salt lost 18·6% of its ammonia in 3 hours at 100° (Found : Cr, 21·4; NH_3, 35·0; Cl, 28·9. $[Cr(NH_3)_5OH]Cl_2,H_2O$ requires Cr, 21·4; NH_3, 35·0; Cl, 29·2%).

Hydroxopentamminochromic bromide separated as a solid mass of pink needles when aquopentamminochromic bromide was dissolved in ammonia, and a little ice-cold alcohol added (Found : Cr, 16·3; NH_3, 26·1; Br, 49·5; H_2O, 3·0. $[Cr(NH_3)_5OH]Br_2,\frac{1}{2}H_2O$ requires Cr, 16·1; NH_3, 26·4; Br, 49·5; H_2O, 2·8%).

Hydroxopentamminochromic iodide was obtained as bunches of minute, pink needles by dissolving 5 g. of aquopentamminochromic iodide in 30 c.c. of concentrated ammonia and adding slowly 100 c.c. of ice-cold alcohol. It was somewhat less soluble than the other salts (Found : Cr, 12·7; NH_3, 20·6; I, 60·9. $[Cr(NH_3)_5OH]I_2,\frac{1}{2}H_2O$ requires Cr, 12·5; NH_3, 20·4; I, 60·9%). When solid potassium iodide was added to a solution of aquopentamminochromic nitrate

in concentrated ammonia, an addition compound of the hydroxo-iodide with potassium iodide was obtained (pink needles).

Hydroxopentamminochromic chromate was obtained by adding the hydroxide solution (55 c.c.) from 4 g. of chloropentamminochromic chloride to 2·5 g. of ammonium chromate dissolved in ammonia. The intense reddish-brown solution was treated with alcohol until a permanent crystalline precipitate just formed (aggregates of thin, brown plates). This was collected and washed with ammoniacal alcohol and ether (Found : Cr, 38·7; NH_3, 31·3. $[Cr(NH_3)_5OH]CrO_4$ requires Cr, 38·5; NH_3, 31·5%).

No reduction in weight occurred when the salt was kept for a fortnight over phosphoric oxide.

Hydroxopentamminochromic Oxalate.—The hydroxide solution from 5 g. of chloropentamminochromic chloride (100 c.c.) was added to 2·92 g. of ammonium oxalate in 100 c.c. of water, when ammonia was immediately evolved. Ammonia solution (10 c.c.) was added, and a considerable excess of alcohol and ether; the precipitate of large, pink needles was readily soluble in water (Found : Cr, 18·6; NH_3, 30·4. $[Cr(NH_3)_5OH]C_2O_4,2H_2O$ requires Cr, 18·7; NH_3, 30·6%).

Hydroxopentamminocobaltic Nitrate.—The following is a more convenient method than that given by Werner (*loc. cit.*) for preparing the pure monohydrated salt. To a filtered solution of 20 g. of aquopentamminocobaltic nitrate in 100 c.c. of concentrated ammonia, 240 c.c. of boiling alcohol are added and the mixture is cooled quickly to prevent separation of an oil. The precipitate is dissolved in ammonia, and to the ice-cold filtered solution cooled alcohol is added drop by drop until crystallisation begins (yield 7 g.) (Found : Co, 19·4; NH_3, 28·1. Calc., Co, 19·5; NH_3, 28·1%).

C. *Electrical Conductivities of Chromammines and Cobaltammines.*

The λ–$C^{1/3}$ *Graph* (see Porter, *Trans. Faraday Soc.*, 1919, **15**, 122).—The electrical conductivities of a large number of salts of bivalent chromammine and cobaltammine kations give, for the concentration range $v = 32$ to $v = 1024$, a rectilinear λ–$C^{1/3}$ graph. This has been found to be the case for hydroxopentamminochromic nitrate, chloride and hydroxide, hydroxopentamminocobaltic nitrate, chloropentamminochromic chloride and bromide, chloropentamminocobaltic sulphate, bromide, chloride and nitrate, nitropentamminochromic chloride (xantho), nitropentamminocobaltic nitrite and chloride (xantho), dinitrotetramminocobaltic nitrate (flavo) and chloride (croceo). It has therefore been concluded that in normal cases the λ–$C^{1/3}$ graph for such salts over this range should be rectilinear and that deviations are due to such

phenomena as polymerisation in concentrated solution, hydration and hydrolysis. This view was supported by the fact that in several cases where deviation was found at 25° the graph was rectilinear at 0° (*e.g.*, chloropentamminochromic bromide, Table III). Further, in cases where this graph is rectilinear, extrapolation to zero concentration by means of the $1/\lambda$–$(C\lambda)^{n-1}$ graph gives concordant values for the mobility of the complex ion, whilst extrapolation of data for the same ion which give a curved λ–$C^{1/3}$ graph leads to a quite different mobility value. Thus for the bivalent hydroxopentamminochromic ion, extrapolation of the conductivity data for the nitrate and chloride gives mobility values 131·6 and 131·9 at 25°, whilst the oxalate and sulphate data, which deviate from the straight-line rule (probably owing to polymerisation in concentrated solution), lead to mobility values 380·9 and 195·0.

The rectilinear λ–$C^{1/3}$ graph does not appear to be suitable for extrapolation of conductivity data to infinite dilution, since accurate data for concentrations less than $\frac{1}{1000}$ (*e.g.*, for potassium chloride) are lower than those required by the graph. For ammines of chromium and cobalt it leads usually to results 6% higher at 25° than those obtained by the $1/\lambda$–$(C\lambda)^{n-1}$ graph.

In many cases at $v = 2000$, and sometimes at higher concentrations, the conductivities of ammines are *higher* than those required by the rectilinear λ–$C^{1/3}$ graph. Such data have been considered to be influenced by decomposition of the complex ion, and have been ignored in calculating λ_∞. They are bracketed in the tables.

The rule does not appear to apply to salts of tervalent complex kations. The λ–$C^{1/3}$ graphs for hexammino-chromic (-cobaltic) and aquopentammino-chromic (-cobaltic) salts are curved. Nevertheless, extrapolation leads to concordant results from different salts of the same ion.

Conductivity Data.—The usual Kohlrausch method was employed, resistances being measured by a standardised Post Office box. An open cylindrical cell of constant 0·1197 was used for the salts. The conductivity water was obtained by a single distillation of distilled water with a little potassium bisulphate, and its specific conductivity varied between $0{\cdot}66 \times 10^{-6}$ and $1{\cdot}1 \times 10^{-6}$ mho, at 0°. Except in the case of hexammino-salts, the method of successive dilutions was not employed. A fresh solution was prepared for each measurement, and its conductivity was determined forthwith. This was particularly necessary in the case of hydroxo-salts, since their conductivity increased rapidly when they were kept in contact with the electrodes.

Table I.

Hydroxopentammino-chromic and -cobaltic Salts.

v is the reciprocal of the concentration in mols. per litre, and λ the molecular conductivity in mhos.

Bracketed data have been ignored in calculating λ_∞.

	$[Cr(NH_3)_5OH]Cl_2$.		$[Cr(NH_3)_5OH](NO_3)_2$.		$[Cr(NH_3)_5OH]SO_4$.	
v.	$\lambda_{0°}$.	$\lambda_{25°}$.	$\lambda_{0°}$.	$\lambda_{25°}$.	$\lambda_{0°}$.	$\lambda_{25°}$.
32	108·8	206·2	106·4	201·5	(59·4)	(117·6)
64	119·0	225·7	115·7	219·4	(69·5)	(132·9)
128	127·5	239·0	124·7	233·6	(82·0)	(158·3)
256	134·9	253·0	132·0	244·3	(94·1)	(181·2)
512	138·8	261·9	138·9	254·2	(108·3)	(208·2)
1024	147·2	274·6	141·4	260·8	(118·9)	(234·0)
2048	—	—	(152·7)	(279·9)	(132·3)	(254·2)

	$[Cr(NH_3)_5OH]C_2O_4$.	$[Co(NH_3)_5OH](NO_3)_2$.	
v.	$\lambda_{25°}$.	$\lambda_{0°}$.	$\lambda_{25°}$.
32	(132·8)	—	196·5
64	(150·4)	—	215·2
128	(169·6)	124·2	229·5
256	(190·0)	132·2	241·5
512	(213·4)	138·4	(253·4)
1024	(235·5)	143·4	(266·2)

Table II.

Hydroxopentamminochromic Hydroxide, $[Cr(NH_3)_5OH](OH)_2$.

α = degree of dissociation.

v	22·53	32·85	42·92	65·70	365·8	∞ (extrapolated
$\lambda_{0°}$	237·8	245·5	250·0	254·1	273·7	283·9
α	83·8	86·5	88·1	89·5	96·4	—

The hydroxide solution was prepared by triturating chloropentamminochromic chloride with moist silver oxide (Christensen, *loc. cit.*), filtering, and washing the oxide with a little ice-cold conductivity water. Air was excluded as much as possible during the preparation, and the conductivity was measured in a stoppered flask-shaped cell. The concentration was determined by an ammonia estimation. The hydroxide prepared from aquopentamminochromic chloride gave similar results. A positive water correction was applied (Lamb and Yngve, *loc. cit.*). The water used was practically "equilibrium water," its specific conductivity being $0·66 \times 10^{-6}$ mho at 0°.

Table III.

Chloropentamminochromic Salts.

	$[Cr(NH_3)_5Cl]Cl_2$.		$[Cr(NH_3)_5Cl]Br_2$.	
v.	$\lambda_{0°}$.	$\lambda_{25°}$.	$\lambda_{0°}$.	$\lambda_{25°}$.
64	123·1	230·3	—	(232·3)
128	131·1	244·5	134·8	(247·7)
256	137·2	255·0	142·1	(261·5)
512	142·3	264·4	146·8	(272·9)
1024	(147·6)	(276·8)	151·2	(280·6)

The conductivity increased rapidly on standing, particularly in the case of the bromide.

TABLE IV.

Aquopentammino-salts.

v	32	64	128	256	512	1024
$\lambda_{0°}$ for $[Cr(NH_3)_5H_2O]Cl_3$	169·5	186·3	203·4	218·4	232·9	(247·8)
$\lambda_{0°}$ for $[Co(NH_3)_5H_2O](NO_3)_3$	163·0	179·0	197·6	212·2	225·9	238·0

TABLE V.

Hexamminochromic Salts.

	$[Cr(NH_3)_6](NO_3)_3$.		$Cr(NH_3)_6Br_3$.		$[Cr(NH_3)_6](NO_3)_3$.		$Cr(NH_3)_6Br_3$.
v.	$\lambda_{0°}$.	$\lambda_{25°}$.	$\lambda_{25°}$.	v.	$\lambda_{0°}$.	$\lambda_{25°}$.	$\lambda_{25°}$.
32	—	307·5	—	512	236·3	439·9	453·5
64	182·6	340·2	355·5	1024	250·0	465·9	480·5
128	201·6	375·3	391·1	2048	260·5	489·8	—
256	219·7	408·0	423·3	4096	269·9	512·3	—

The conductivities for hexamminochromic nitrate at 25° are considerably higher than those recorded by Werner and Miolati (*loc. cit.*).

Ionic Mobilities.—The conductivity at infinite dilution has been obtained in every case from the $1/\lambda$–$(C\lambda)^{n-1}$ graph (Noyes and Coolidge, *Carnegie Inst. Pub.*, **63**, 50).

Hydroxopentamminochromic ion. The data for the chloride and nitrate (Table I) give mobility 73·0 and 73·5 (n = 1·56 and 1·52) at 0° and 131·9 and 131·6 (n = 1·60) at 25°. The means of these closely concordant values are adopted in Table VI. The data for hydroxopentamminochromic hydroxide give mobility 73·9 at 0°, in excellent agreement with the figure derived from the salts.

Hydroxopentamminocobaltic ion. The data for the nitrate (Table I) give mobility 76·6 at 0° (n = 1·50) and 131·0 at 25° (n = 1·60).

Chloropentamminochromic ion. The data in Table III give the ionic mobility as 75·2 and 76·8 (chloride and bromide) at 0° (n = 1·50) and as 139·7 (chloride) at 25° (n = 1·50). The data of Werner and Miolati (*loc. cit.*) for the chloride at 25° give a slightly lower value (138·4). The lower figure 75·2 at 0° has been adopted, since the bromide results are probably affected by hydration.

Chloropentamminocobaltic ion. The data of Werner and Miolati (*loc. cit.*; *Z. physikal. Chem.*, 1896, **21**, 235) for chloropentamminocobaltic salts at 25° give an ionic mobility 3·5% higher than that of the corresponding chromammine ion, but extrapolation of the more recent results obtained by Harkins, Hall, and Roberts (*J. Amer. Chem. Soc.*, 1916, **38**, 2643) for the chloride gives values 74·8 at 0° and 140·8 at 25° (n = 1·60 and 1·82). These are the values adopted in Table VI.

Aquopentammino-chromic and *-cobaltic ions* at 0°. The data of Table IV give mobilities 174·3 ($n = 1·40$) and 161·7 ($n = 1·44$). The latter agrees well with the estimated value of 160 given by Lamb and Yngve (*loc. cit.*).

Hexamminochromic ion. The data of Table V give mobility 180·0 at 0° ($n = 1·46$) and 369·6 and 370·8 (nitrate and bromide) at 25° ($n = 1·42$ and 1·40).

The diminution in mobility of the complex ion at 0° on replacing one ammonia molecule of the hexammine by water is 5·7 in the chromammine, 5·3 in the cobaltammine series (see Table VI).

The values employed for the mobilities of the anions at 0° and 25° were Cl′, 41·1 and 75·5; Br′, 43·1 and 77·8; NO_3', 40·4 and 70·6; OH′, 105·0 (0°); $\frac{1}{2}SO_4''$, 78·0 (25°); $\frac{1}{2}C_2O_4''$, 72·7 (25°).

The ionic mobilities of the complex kations are collected in Table VI. Those indicated by an asterisk are taken from the table given by Lamb and Yngve (*loc. cit.*). Q = valency of kation.

TABLE VI.

Kation.	$\Lambda_{0°}$.	$\Lambda_{0°}/Q^2$.	$\Lambda_{25°}$.	$\Lambda_{25°}/Q^2$.
1 : 2-$[Co(NH_3)_4(NO_2)_2]^{\cdot}$	18·1*	18·1	36·3*	36·3
1 : 6-$[Co(NH_3)_4(NO_2)_2]^{\cdot}$	17·9*	17·9	36·1*	36·1
$[Cr(NH_3)_5OH]^{\cdot\cdot}$	73·3	18·3	131·8	33·0
$[Co(NH_3)_5OH]^{\cdot\cdot}$	76·6	19·2	131·0	32·8
$[Cr(NH_3)_5Cl]^{\cdot\cdot}$	75·2	18·8	139·7	34·9
$[Co(NH_3)_5Cl]^{\cdot\cdot}$	74·8	18·7	140·8	35·2
$[Cr(NH_3)_6]^{\cdot\cdot\cdot}$	180·0	20·0	370·2	41·1
$[Co(NH_3)_6]^{\cdot\cdot\cdot}$	167·0*	18·6	327·0*	36·3
$[Cr(NH_3)_5H_2O]^{\cdot\cdot\cdot}$	174·3	19·4	—	—
$[Co(NH_3)_5H_2O]^{\cdot\cdot\cdot}$	161·7	18·0	314·0*	34·9

The mobilities of corresponding chromammine and cobaltammine bivalent ions are practically identical.

The marked increase in mobility of the complex ions with increase of valency has no parallel among ordinary metallic kations. If the mobility is divided by the square of the valency, an approximate constant is obtained throughout the table, showing that the mobility is proportional to the square of the ionic charge. The mean values of Λ/Q^2 for univalent, bivalent and tervalent ions are 18·0, 18·8 and 19·0 at 0° and 36·2, 34·0 and 37·4 at 25°. For metallic kations, Λ/Q is approximately constant.

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CCLXXXVII.—*Electrometric Studies of the Precipitation of Hydroxides. Part I. Precipitation of Magnesium, Manganous, Ferrous, Cobalt, Nickel, and Thorium Hydroxides by Use of the Hydrogen Electrode.*

By Hubert Thomas Stanley Britton.

No satisfactory system of classifying the metals according to the strengths of their hydroxides has yet been evolved, although it is this property which underlies the general chemical character of the elements and also many analytical separation processes. Measurements of the basic strength by determinations of electromotive force, of heats of formation of oxides and salts, of dissociation pressures of sulphates at different temperatures, and of the hydrolysis of various salts in solution have led to different arrangements. The arrangement in the order of the dissociation constants of the hydroxides as calculated from hydrolysis data is not altogether satisfactory, for in the majority of cases sufficiently accurate measurements cannot be made.

Curiously enough, the order of the precipitation of the hydroxides by the gradual addition of alkali has received no serious attention, except with regard to the separation of the rare-earths. Hildebrand's work (*J. Amer. Chem. Soc.*, 1913, **35**, 847) in this connexion has been repeated and extended by the present author. A definite hydrogen-ion concentration, within narrow limits, has to be attained before the precipitation of any particular hydroxide can take place. This would be expected from a consideration of the "solubility product." An insoluble hydroxide, MOH, attains equilibrium with undissociated molecules and ions in solution, thus :

$$\text{MOH (solid)} \rightleftharpoons \text{MOH (undissociated)} \rightleftharpoons \text{M}^{\cdot} + \text{OH}'.$$

The "solubility product" $= [\text{M}^{\cdot}][\text{OH}'] = [\text{M}^{\cdot}]K_w/[\text{H}^{\cdot}]$, where $K_w = [\text{H}^{\cdot}][\text{OH}']$. The precipitation of the hydroxide thus depends on the concentration of both the metal- and the hydrogen-ions. In ordinary analytical operations, the concentrations of the metal ions do not vary to any considerable extent and consequently precipitation depends largely on the hydrion concentration. The hydrion concentrations necessary for the precipitation of a large number of hydroxides, which have now been determined, constitute a suitable basis for the classification of the hydroxides. The order is "parallel" to the increasing magnitude of the solubility products, but whether it is that of the basic strengths cannot be stated with certainty; this can be so only if the concentration of undissociated

molecules is the same for each hydroxide—a point about which nothing is known.

The Hydrogen Electrode.

For titrations involving the separation of precipitates, the Hildebrand form of hydrogen electrode was found to be the most convenient; the hydrogen, obtained from a supply under pressure (*e.g.*, a cylinder), could be passed through the solutions at such a rate that thorough mixing could be ensured, and its rapid passage through the electrode tended to free the platinum black from gases such as carbon dioxide and ammonia which were apt to be occluded, and also completely removed any dissolved oxygen from the solutions. The titrations were carried out in the manner already described (J., 1924, **125**, 1576). The uncertain behaviour of the hydrogen electrode (see *loc. cit.*) is no doubt responsible for many of the conflicting statements in the literature, especially with reference to its use in alkaline solutions. Thus Johnson (*Trans. Amer. Electrochem. Soc.*, 1902, **1**, 187) found the electrode to be sluggish, and Allmand (J., 1909, **95**, 2151) concluded that it was untrustworthy in alkaline solutions. Everything depends, however, on the electrode, its method of preparation and its use, for some electrodes are as satisfactory in alkaline as in acid solutions. Efficient electrodes tend to improve with continuous use, and in a few cases electrodes have remained good over a period of three months.

In precipitation reactions the efficiency of the electrode sometimes depends on the nature of the precipitate; the finer the precipitate the less likely is the electrode to give satisfactory results. In general, precipitates merely render the electrode sluggish. No electrode functions in the presence of precipitated sulphur, but this may be due, not to the fineness of the precipitate, but to interaction between the hydrogen and the sulphur.

The hydrogen electrode has some limitations, but these are not so extensive as is generally stated. It can be used in presence of reducible substances such as nitrates and chromates (compare Britton, *loc. cit.*) if the solution is dilute. No electrode gave complete satisfaction in presence of sulphites; in some titrations, however, the initial readings appeared to be approximately true.

The hydrogen electrode is, of course, inapplicable in solutions containing metals more noble than hydrogen. Moreover, Denham and Allmand (J., 1908, **93**, 424) and Denham (*ibid.*, p. 833) found that the hydrogen electrode behaves anomalously in solutions of lead, cadmium, and univalent thallium salts, owing to catalytic reduction of the kations to a state of lower valency. These observations have been confirmed by the author. It was, however,

thought just possible that by having a suitable layer of platinum black, electrodes might be prepared which would not react with these kations; but numerous attempts to do so were fruitless. In view of the fact that the hydrogen electrode is affected by lead ions in solution, it is remarkable that the lead which is usually deposited with the platinum black does not render the electrode useless; in fact, its presence in the latter seems to increase its efficiency as far as titration work is concerned. Denham and Allmand proved conclusively that lead in the electrode is absolutely without any deleterious effect, for they deposited electrolytically a layer of lead on a hydrogen electrode and found that the electrode still gave correct results.

Previous Investigations with the Hydrogen Electrode in Inorganic Chemistry.

The only observations relating to reactions similar to those now described appear to have been made by Bjerrum (*Z. physikal. Chem.*, 1907, **59**, 336; 1910, **73**, 724), Sand and Grammling (*ibid.*, 1908, **62**, 1), Hildebrand and Harned (Orig. Com., 8th Internat. Cong. Appl. Chem., 1912, **1**, 217), Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 847), Blum (*ibid.*, p. 1499; 1916, **38**, 1282), and Hildebrand and Bowers (*ibid.*, 1916, **38**, 785).

Denham (J., 1908, **93**, 41; *Z. anorg. Chem.*, 1908, **57**, 388) employed the electrode extensively for the determination of the hydrolysis of salts. Steady *E.M.F.*'s were obtained in some cases; in others, they oscillated haphazardly from day to day, showing in the case of *M*/64-thorium sulphate solution that the degree of hydrolysis, calculated to the second step [*i.e.*, to $Th(OH)_2SO_4$] varied from 23 to 59%. The author has not observed any such changes with *M*/100-solutions of either the sulphate, chloride or nitrate at 15°, even after the solutions had been kept in stoppered bottles for several weeks. The following data show that the three salts are almost equally hydrolysed, the extent being half the lowest value obtained by Denham for *M*/64-thorium sulphate solution.

Salt.	*E.M.F.* of H_2 electrode against normal calomel.	Percentage hydrolysis calc. to $Th(OH)_4$.
Nitrate	0·434	5·70
Chloride	0·435	5·47
Sulphate	0·437	5·04

Electrometric Titrations with the Hydrogen Electrode.

(1) *Effect of Concentration, Anion, and Precipitant on the Hydrogen-ion Concentrations required for the Precipitation of Hydroxides.*—Experiments were carried out to see what was the effect of change

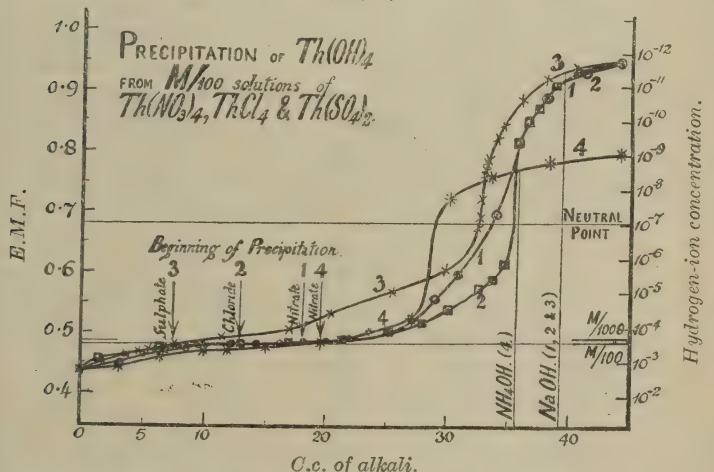
in concentration of salt. The following table gives the p_H values at which thorium hydroxide began to be precipitated by $N/10$-sodium hydroxide at 15° from solutions of thorium nitrate ranging in concentration from $M/1000$ to $M/100$.

Concentration.	*E.M.F.* of H_2 electrode against normal calomel.	p_H.
$0{\cdot}001M$	0·489	3·60
$0{\cdot}002M$	0·488	3·58
$0{\cdot}01M$	0·487	3·57

The difference in p_H is thus very small and this range of concentrations covers those usually employed in analytical work.

Hildebrand found that the p_H's required for the precipitation of neodymia and praseodymia from nitrate solutions were widely

FIG. 1.



(0·1016 N-NaOH, *curves* 1, 2 *and* 3. 0·1115 N-NH_4OH, *curve* 4).

different from those required in the case of chloride solutions, and he attributed this difference to the nature of the anion (see Part III). The effect of the anion and of the nature of the precipitant has been studied more fully in the case of thorium salt solutions, and again precipitation commenced at the same p_H in all cases (Fig. 1). Curves 1, 2, and 3 represent the titrations of 100 c.c. of $M/100$-solutions of thorium nitrate, chloride, and sulphate respectively, with $0{\cdot}1016N$-sodium hydroxide, and curve 4 that of 100 c.c. of $M/100$-thorium nitrate with $0{\cdot}1115N$-ammonium hydroxide, at 15°. The commencement of precipitation, *i.e.*, the first appearance of turbidity, is shown by arrows. As a rule, the *E.M.F.*'s were steady (in some cases an hour elapsed before the next reading was taken),

but they were not always so in those stages of the titration which indicated the rapid changes in hydrion concentration occurring at the end of the precipitation. The last section of curve 1 represents a gradual diminution in hydrion concentration and the readings were stationary during the intervals (5 to 15 minutes) allowed for the attainment of equilibrium. Curve 2, chloride, shows a sudden yet well-defined change, but in the case of the thorium sulphate titration (curve 3) the change was irregular and long periods were necessary before constant readings were obtained. Appreciable amounts of alkali had to be added before the commencement of precipitation, and thereafter, in the case of the nitrate and the chloride solutions, there was a distinct tendency for a constant p_H to be maintained during the addition of the greater portion of the alkali. It is probable that this corresponds to the separation of a precipitate of uniform composition.

In neither case was thorium hydroxide precipitated as such. Fig. 1 shows that precipitation was complete and the mother-liquors had become alkaline some time before the stoicheiometrical quantities of alkali had been added. The following table gives the amounts of alkali which were added before precipitation ensued and the amounts of alkali which had to be added before the solutions became neutral (p_H 7).

Curve.	Solution and precipitant.	Precipitation began: p_H.	Precipitation began: Equivs. of alkali.	Equivs. of alkali required for neutrality.
1	$Th(NO_3)_4$ and NaOH	3·57	1·85	3·43
2	$ThCl_4$ and NaOH	3·51	1·30	3·58
3	$Th(SO_4)_2$ and NaOH	3·53	0·78	3·31
4	$Th(NO_3)_4$ and NH_4OH	3·57	2·21	3·24

The last column of the above table shows that the precipitate formed in each titration was basic, being somewhat less so when the precipitant was ammonia. Thus the amount of precipitant required to render the solution neutral in titration No. 4 indicates that the composition of the precipitate was $Th(OH)_{3·24}(NO_3)_{0·76}$, whereas in No. 1, where sodium hydroxide was used, it was $Th(OH)_{3·43}(NO_3)_{0·57}$. The protracted inflexions produced during the last stages of precipitation show that the precipitates at first formed were less basic and suffered some decomposition on further addition of alkali. This seems to have taken place readily in the cases of the nitrate and the chloride, but the slowness with which apparent equilibrium was attained in the second part of the sulphate titration indicates that the basic sulphate was undergoing hydrolysis with much greater difficulty. It seems almost unnecessary to say that the amounts of acid radical retained by these precipitates

were too great to be accounted for by adsorption from such dilute solutions. These precipitates were not completely decomposed even when excess of alkali was added.

Halla (*Z. anorg. Chem.*, 1912, **79**, 260) made a similar observation with thorium nitrate solutions. He found that at room temperature the solution became alkaline to phenolphthalein on the addition of 3·54 equivalents of potassium hydroxide, and on boiling, with 3·60 equivalents.

Another remarkable fact arising from these titrations is that alkali ranging in amounts from 0·78 to 2·21 equivalents to one molecule of thorium salt had to be added before the appearance of a precipitate. These amounts, which vary with the nature of the anion and the precipitant, do not permit of a guess as to the way in which the thorium hydroxide, or basic complex, is held in solution until the attainment of the p_H requisite for precipitation. According to Ordway (*Amer. J. Sci.*, 1858, **26**, 197), Berzelius observed that when alkali was added to a thorium sulphate solution precipitation was delayed owing to the formation of what appeared to be *un soussel soluble*. Ordway directed attention to several other examples of "soluble basic salt" formation. It will be shown in the course of this series of papers that these so-called soluble basic salts exert a pronounced influence on some of the reactions of the metals of which they are characteristic. It is surprising that "soluble basic salts" are generally formed by those metals the valencies of which are greater than two, although this is the case neither with the tervalent rare-earths nor with bivalent beryllium, which has a remarkable property of forming these basic solutions.

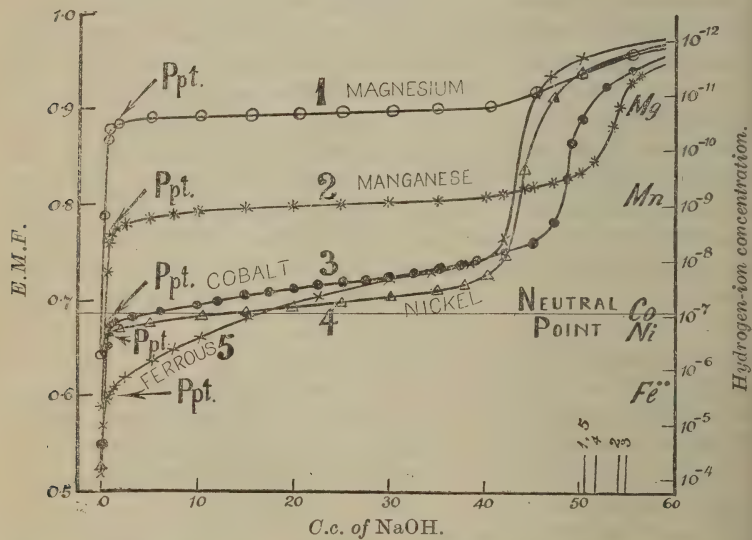
(2) *The Precipitation of the Hydroxides of Magnesium, Manganese, Cobalt, Nickel, and Ferrous Iron.*—The following table gives particulars of the solutions used in typical titrations, together with the amount of alkali required to cause incipient precipitation. The courses of the titrations are shown in Fig. 2.

Titration and curve No.	Temp.	Solution titrated: 100 C.c.	Normality of NaOH.	C.c. of NaOH theoretically required.	Precipitation first began		
					E.M.F.	p_H.	C.c. of NaOH.
1	16°	0·025*M*-$MgSO_4$	0·0990	50·5	0·885	10·49	1·6
2	18	0·024*M*-$MnCl_2$	0·0900	54·0	0·770	8·41	1·0
3	18	0·0247*M*-$CoCl_2$	0·0900	54·8	0·676	6·81	0·9
4	17	0·025*M*-$NiCl_2$	0·0967	51·7	0·666	6·66	0·6
5	17	0·025*M*-$FeSO_4$	0·0990	50·5	0·599	5·49	0·8

In contrast with the thorium salt titrations, the first few drops of sodium hydroxide caused a rapid diminution in hydrion concentration until a value was obtained at which precipitation commenced. Thereafter, precipitation proceeded with very little change

in p_H until the separation was nearly complete. The titration of ferrous sulphate solutions was a matter of some difficulty. As is well known, manganous and ferrous hydroxides on exposure to air readily become oxidised, and consequently the titrations involving their precipitation were performed in vessels which were stoppered as far as possible. Even so, it was not possible to prevent some oxidation from taking place, although plenty of hydrogen was passing through the solutions. The curves, however, were reproducible and there is little doubt that the voltage readings indicated correctly the changes in hydrion concentration. Further support

FIG. 2.



for the belief that the electrodes were behaving normally may be found in the following observations. Atkins (*Trans. Faraday Soc.*, 1923, **18**, 310) found colorimetrically that the precipitation of manganous hydroxide from manganous chloride solutions took place between p_H 8·6 and 9·2 and of ferrous hydroxide from ferrous sulphate solutions between p_H 5·1 and 7·6. Patten and Mains (*J. Assoc. Off. Agric. Chem.*, 1920, **4**, 233) gave p_H 5·5 to 6·0 for ferrous hydroxide.

Precipitation was again complete in each case some time before the theoretical amount of alkali had been added. Curve No. 1, magnesium sulphate, shows that the final inflexion began when 1·64 equivalents of sodium hydroxide had been added The gradual slope of the inflexion was evidently due to the partial decomposition of the basic sulphate, originally precipitated. A similar inflexion,

but steeper, took place in magnesium chloride titrations. Hildebrand and Harned (*loc. cit.*) and Hildebrand (*loc. cit.*) have also studied by means of the hydrogen electrode the precipitation of magnesium hydroxide and have suggested that the electrometric titration of hydrochloric acid solutions of dolomite might be used for the estimation of the magnesia with an accuracy of about 1%, despite the fact that the values obtained by them showed a variation of 5%. The difficulty is that magnesium hydroxide is not precipitated simply from either chloride or sulphate solutions to give sharp inflexions, but indefinite basic precipitates are formed which give poorly defined inflexions; this renders it impossible to assign a point on the curve which exactly corresponds to the neutralisation of all the acid which was originally combined with the magnesium hydroxide. According to Kolthoff (*Rec. trav. chim.*, 1922, **41**, 787), Pinkof (Thesis, Amsterdam, 1919, p. 34) has investigated the electrometric estimation of magnesia by means of the Hg|HgO|Alkali electrode, but obtained unsatisfactory inflexions, even when an excess of alkali was added and the free alkali afterwards titrated. Kolthoff recommended shaking the magnesium salt solution with an excess of alkali and allowing to stand so as to render the decomposition of the basic salt as complete as possible before titration.

Precipitation was complete from (*a*) manganous chloride solution —curve 2—on the addition of about 1·93 equivalents of sodium hydroxide, (*b*) cobalt chloride solution—curve 3—1·75 equivalents, (*c*) nickel chloride solution—curve 4—1·66 equivalents, and (*d*) ferrous sulphate solution—curve 5—1·71 equivalents. Pickering (J., 1907, **91**, 1981) observed that complete precipitation had taken place from ferrous sulphate solutions at the point where they became alkaline to phenolphthalein, and this was when sodium hydroxide had been added in amounts which varied from 1·77 to 1·86 equivalents. He considered this sufficient justification for the assertion that the precipitate was a definite basic salt, $10FeO,SO_3$. In the present titration the alkali required was somewhat less, probably owing to the slowness with which it was added (a period of 2 hours), which caused the precipitation of a sulphate less basic than Pickering's.

Although basic precipitates were always produced, it is possible to calculate from the curves the values of the solubility products of the hydroxides, which are in good agreement with those obtained by other methods. As a rule, precipitation began somewhere near the point of the first inflexion, although often at a p_H which was a little less than that at which the main precipitation took place. This was probably due to the precipitate having been formed at a point in the solution where the precipitation value of p_H had been temporarily exceeded, and time not having been allowed for its

re-solution. If, therefore, the two straight portions of the curve be produced, it is probable that the point of intersection corresponds more nearly to the amount of alkali which had to be added to produce incipient precipitation, and also to the actual hydrion concentration at which precipitation under ideal conditions would commence. This point represents the limiting conditions necessary to form a precipitate. The concentration of metal ions can be calculated from the amount of alkali, and K_w at 18° being $0{\cdot}73 \times 10^{-14}$, the concentration of hydroxyl ions can be found. Columns 2 and 5 in the following table give the co-ordinates of these points for the curves shown in Fig. 2.

No.	*E.M.F.*	p_H.	p_{OH}.	C.c. of NaOH.	$C_{M^{\cdot\cdot}} \times 10^4$.	$[Me^{\cdot\cdot}][OH']^2$.
1	0·892	10·61	3·52	0·5	2·5	$2{\cdot}3 \times 10^{-11} = [Mg^{\cdot\cdot}][OH']^2$
2	0·794	8·85	5·27	1·0	4·5	$1{\cdot}3 \times 10^{-14} = [Mn^{\cdot\cdot}][OH']^2$
3	0·680	6·92	7·22	1·0	4·5	$1{\cdot}6 \times 10^{-13} = [Co^{\cdot\cdot}][OH']^2$
4	0·675	6·81	7·32	0·8	3·9	$8{\cdot}7 \times 10^{-19} = [Ni^{\cdot\cdot}][OH']^2$
5	0·615	5·77	8·37	0·6	3·0	$4{\cdot}5 \times 10^{-21} = [Fe^{\cdot\cdot}][OH']^2$

The method is, of course, open to the objections (*a*) the difficulty of estimating accurately the amount of alkali required, and (*b*) the fact that basic salts were actually precipitated which may have had some effect on both the hydroxyl- and the metal-ion concentrations.

As a result of their conductivity determinations at 18°, Kohlrausch and Rose (*Z. physikal. Chem.*, 1893, **12**, 241) obtained a value of $3{\cdot}4 \times 10^{-11}$ for the solubility product of magnesium hydroxide. Calculation from the solubility data of Lovén (*Z. anorg. Chem.*, 1896, **11**, 404) gives values ranging from $2{\cdot}7$ to $9{\cdot}2 \times 10^{-11}$. These values are of the same order as the one obtained in this work.

Sackur and Fritzmann (*Z. Elektrochem.*, 1909, **15**, 845) carried out a conductimetric titration of manganous sulphate with barium hydroxide and obtained the value 4×10^{-14} for $[Mn^{\cdot\cdot}][OH']^2$, in agreement with the value $1{\cdot}3 \times 10^{-14}$, given in the table.

No values appear to have been found for the hydroxides of cobalt and nickel. Those reported for ferrous hydroxide are very discrepant; Müller (*Z. Elektrochem.*, 1908, **14**, 77) records $1{\cdot}64 \times 10^{-14}$ at 18°, and Krassa (*ibid.*, 1909, **15**, 491) $8{\cdot}7 \times 10^{-14}$. On the other hand, Müller ("Das Eisen und seine Verbindungen," 1917, pp. 180, 199) calculated, from Bodländer's formula (*Z. physikal. Chem.*, 1898, **27**, 66), which involves the heat of formation of ferrous hydroxide and the decomposition potentials of the two ions, the value $2{\cdot}51 \times 10^{-21}$, which is in remarkable agreement with the value $4{\cdot}5 \times 10^{-21}$ given by titration. The observations of Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 847) on the titration of

ferrous sulphate are in no way similar to the present ones, for the precipitation of ferrous hydroxide did not commence until a considerable proportion of alkali had been added.

These curves throw considerable light on the function of ammonium salts in preventing the precipitation of certain hydroxides. The addition of ammonium salts to ammonia may be such that the p_H is depressed below the precipitation value of either magnesium or manganous hydroxide. The approximate hydrogen-ion concentration of a solution containing ammonium hydroxide and ammonium chloride is given by

$$[H^{\cdot}] = \frac{[NH_4Cl]K_w}{[NH_4OH]K_{NH_4OH}},$$

where $K_w = 10^{-14\cdot14}$ and $K_{NH_4OH} = 10^{-4\cdot64}$ at 18°.

If ammonium chloride is regarded as being completely dissociated, the minimum number of molecules of ammonium chloride to be added to each molecule of ammonia to increase the hydrion concentration to that required just to start precipitation of (*a*) magnesium hydroxide is 0·08, (*b*) manganous hydroxide, 4·5, (*c*) cobaltous hydroxide, 380, and (*d*) hydroxides of nickel and ferrous iron, still more. In analytical processes, the condition for the prevention of the precipitation of the hydroxides of magnesium and manganese is easily satisfied, but the sole cause of the partial or non-precipitation of the other hydroxides is the magnitude of the quantities of ammonium chloride that must be added. Herz (*Z. anorg. Chem.*, 1900, **23**, 227) believed that the behaviour of ammonium chloride in depressing the hydroxyl-ion concentration was also the cause of the non-precipitation of zinc hydroxide, but, as will be shown in the next paper, zinc hydroxide is precipitated while the mother-liquor is still very slightly acid and consequently its precipitation could not be affected by the ammonium salt in the same way as in the foregoing instances. It is more probable, as has been suggested by several investigators, that it is the ammonia itself which maintains the hydroxides of zinc, cobalt, and nickel in solution through the formation of complex ions. No explanation, however, appears to be forthcoming to account for the small effect which ammonium chloride has on the precipitation of ferrous hydroxide. The researches of Lovén (*loc. cit.*), Treadwell (*Z. anorg. Chem.*, 1903, **37**, 326), and Herz and Muhs (*ibid.*, 1904, **38**, 138) have all led to the conclusion, given more directly by these titrations, regarding the influence of ammonium salts in preventing the precipitation of magnesium hydroxide. There are no grounds for attributing it to the formation of a complex magnesium anion—an explanation which is still to be found in some text-books.

Summary.

(1) The reactions between sodium hydroxide and solutions of magnesium, bivalent manganese and iron, cobalt, nickel and thorium salts have been studied by means of the hydrogen electrode.

(2) In every case, the precipitate of hydroxide contained an appreciable proportion of unattacked acid radical.

(3) Hydrogen-ion concentrations, which are peculiar to the various hydroxides, are independent of both the anion and the precipitant, and are only slightly influenced in dilute solutions by changes in concentration of the metallic salts, have to be attained before any particular hydroxide can be precipitated.

(4) The dependence of these hydrion concentrations on the solubility products of the different hydroxides has been shown by calculation, from the respective titration curves, of solubility products which are in agreement with values obtained by other methods.

(5) The well-known effect of ammonium salts in preventing the precipitation by ammonium hydroxide of magnesium and manganous hydroxides has been shown, more directly than has been the case hitherto, to be due to the incapacity of ammonia to produce hydrogen-ion concentrations which are less than those necessary for the precipitation of the respective hydroxides, provided that the ratio of ammonium salt to ammonia be sufficiently large.

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Imperial College of Science and Technology,
South Kensington. [*Received, June 9th*, 1925.]

CCLXXXVIII.—*Electrometric Studies of the Precipitation of Hydroxides. Part II. The Precipitation of the Hydroxides of Zinc, Chromium, Beryllium, Aluminium, Bivalent Tin and Zirconium by Use of the Hydrogen Electrode, and their Alleged Amphoteric Nature.*

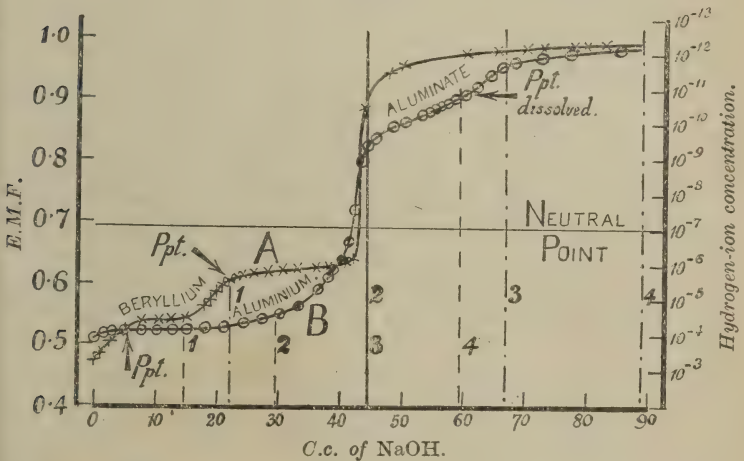
By Hubert Thomas Stanley Britton.

In this part of the work, those hydroxides, including zirconium hydroxide, which are generally supposed to have both basic and acidic properties have been studied, first with respect to their

precipitation, and secondly with respect to the changes in hydrion concentration produced when they react with sodium hydroxide in various proportions. It is very doubtful whether zirconium hydroxide is amphoteric; Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 847), however, has obtained electrometric evidence for the existence of zirconates.

Aluminium and Beryllium Hydroxides.—Hildebrand (*loc. cit.*) and Blum (*ibid.*, p. 1499) observed that on titrating aluminium salt solutions with sodium hydroxide, using the hydrogen electrode, a characteristic inflexion was produced in the curve which corresponded to the formation of sodium monoaluminate. It was

FIG. 1.



therefore decided to see if inflexions were also given in the titration curves of the other so-called amphoteric hydroxides.

The following two solutions (100 c.c.) were titrated at 17°, and the *E.M.F.*'s of the hydrogen electrode compared with that of the normal calomel electrode, saturated potassium chloride solution being the junction liquid. The curves are given in Fig. 1.

Soln. titrated.	Normality of NaOH.	C.c. of NaOH theoretically required.	Precipitate first appeared. *E.M.F.*	p_H.	C.c. of NaOH.
0·00667*M*-$Al_2(SO_4)_3$	0·090	44·4	0·521	4·14	5·0
0·02*M*-$BeSO_4$	0·090	44·4	0·610	5·69	23·0

Neither Hildebrand nor Blum directed attention to the fact that precipitation was complete before the theoretical amount of alkali had been added. The present titration (Fig. 1) shows that precipitation did not begin until 5 c.c. of alkali had been added,

when the dissolved aluminium sulphate had attained the composition given by the formula $Al_2O_3,2{\cdot}65SO_3$, and was complete when 42·2 c.c. (= 5·7 equivalents to 1 mol. of Al_2O_3) of alkali had been added, thereby showing that the basic precipitate contained $Al_2O_3,0{\cdot}15SO_3$. Williamson (*J. Physical Chem.*, 1923, **27**, 284) found that the precipitates formed by the addition of 2 to 4 equivalents of sodium hydroxide were of nearly constant composition and approximated to $Al_2O_3,0{\cdot}6SO_3,3H_2O$. Miller (*U.S. Public Health Reports*, 1923, **38**, 1995) investigated the precipitation from aluminium sulphate solutions by means of alkali and measured the variation in the p_H of the mother-liquors colorimetrically. For additions of sodium hydroxide up to 5 equivalents, the precipitates were similar in composition to those of Williamson, the p_H varying from 4·0 to 5·5. The curve shows that this was the variation in hydrion concentration during the addition of the first 5 equivalents of sodium hydroxide (= 37·0 c.c.) and save for that portion of the curve which corresponds to the addition of the fifth equivalent—between 29·6 and 37·0 c.c.—the gradient of the curve is both uniform and gradual such as would be expected if the precipitate formed were of uniform composition. Miller found that the greatest insolubility of the precipitate occurred when 5·5 equivalents of sodium hydroxide had been added and a hydrion concentration between $10^{-6{\cdot}7}$ and 10^{-7} had been reached. This state corresponds to the maximum decomposition of the basic sulphate which was first precipitated.

The amount of alkali required to form sodium aluminate, $NaAlO_2$, was 59·2 c.c., and although a trace of precipitate remained undissolved when that amount had been added, the solution became quite clear on the addition of a further 2 c.c. of alkali. During the process of re-solution of the aluminium hydroxide, there was a marked depression in the hydroxyl-ion concentration as shown by the inflexion of the curve which was similar to that previously observed by Hildebrand and by Blum. This inflexion seems to provide definite evidence for the existence of an aluminate in solution. As will be shown, in no other instance of the so-called amphoteric hydroxides is such an inflexion produced. Incidentally, in all cases the amounts of alkali required to dissolve the hydroxides, except that of zirconium, which does not dissolve, are considerably in excess of that denoted by the formulæ of the salts which have been said to be formed. In the case of aluminium hydroxide only is the amount of alkali required for its re-solution approximately equal to that suggested by the formula, $NaAlO_2$, and is also independent of the concentration of the sodium hydroxide used (compare Britton, *Analyst*, 1921, **46**, 363). It is possible that the other

hydroxides may be acidic in their behaviour towards alkalis, but to so small an extent that the hydrogen-ion concentration of the alkali solution is scarcely affected.

The other curve in Fig. 1, which represents the titration of beryllium sulphate, has two distinct sections in the acid zone. Precipitation was delayed until the beginning of the second section had been reached, when 1·04 equivalents of sodium hydroxide had been added. Thus the beryllium sulphate had to be rendered basic to the extent shown by the formula $BeSO_4,Be(OH)_2$, before a precipitate began to separate. Although the beryllium sulphate had become so basic, the solution remained perfectly clear and betrayed no sign of colloidality. Calculation from the analytical data of Parsons (*J. Amer. Chem. Soc.*, 1904, **26**, 1433) for the liquid phases saturated with respect to basic beryllium sulphate reveals that the liquid phases all contained soluble basic sulphate whose composition appeared to be independent of the concentrations used, *viz.*, from 0·38 to 2·86% of beryllium oxide. The average ratio of beryllium oxide to sulphate in twenty-two liquid phases was $BeO,0{\cdot}547SO_3$, the ratio appearing to have varied haphazardly from 0·508 to 0·622 mol. of SO_3. (In making these calculations the analyses of two liquid phases were discarded, for it seemed certain that the solutions could not have attained anything approaching equilibrium.) Parsons' solution thus contained a little less beryllium hydroxide than was the case with this solution while undergoing titration. The fact that there was a marked inflexion in the hydrion curve just at the stage when the first half of the stoicheiometric amount of sodium hydroxide had been added seems to indicate some fundamental difference between the first and second hydroxyl groups of beryllium hydroxide which gives rise to the formation of soluble basic salts in which the first beryllium valency is attached to the weaker hydroxide group. It must be stated, however, that concentrated solutions of beryllium sulphate can be rendered still more basic to the extent of 2 mols. of $Be(OH)_2$ to 1 mol. of $BeSO_4$. It is probable, whether the basic sulphate does or does not exist in solution as a definite chemical compound, that the solution is mainly colloidal in nature, in spite of the fact that it is clear and is not coagulated by electrolytes. The colloidal aggregates of beryllium hydroxide which probably exist in some type of combination with the sulphate groups appear to be capable of ionisation, although to a less extent than would have been the case had the sulphate radicals been united with beryllium simply. If these basic solutions happen to be examples of colloidal electrolytes, it would be expected that the dissolution of beryllium hydroxide in a beryllium sulphate solution, being

brought about by the formation of aggregates of the beryllium hydroxide and the beryllium sulphate, would be accompanied either by a diminution in the number of osmotically active particles, partly present as an ionisable colloid and partly in true solution, or, in the extreme and improbable case, by no change in the number. Some support for this view is to be found in the observations of Parsons, Robinson, and Fuller (*J. Physical Chem.*, 1907, **11**, 651), who found that the effect of dissolving beryllium hydroxide in solutions of beryllium sulphate was to raise the freezing point and to reduce the conductivity.

Precipitation of beryllium hydroxide was complete when 1·91 equivalents of sodium hydroxide (= 42·5 c.c.) had been added, the precipitate containing therefore $BeO,0{\cdot}045SO_3$. The contents of the solid phases obtained by Parsons (*vide supra*) in his study of the 25°-isotherm of the ternary system $BeO–SO_3–H_2O$ show that they contained between 0·034 and 0·048 mol. of SO_3 to each mol. of BeO.

The re-solution of the beryllium hydroxide was not complete when 90 c.c. of alkali had been added, which amount was a little in excess of that required to form sodium beryllate, Na_2BeO_2, neither did the titration curve give any indication that combination had taken place.

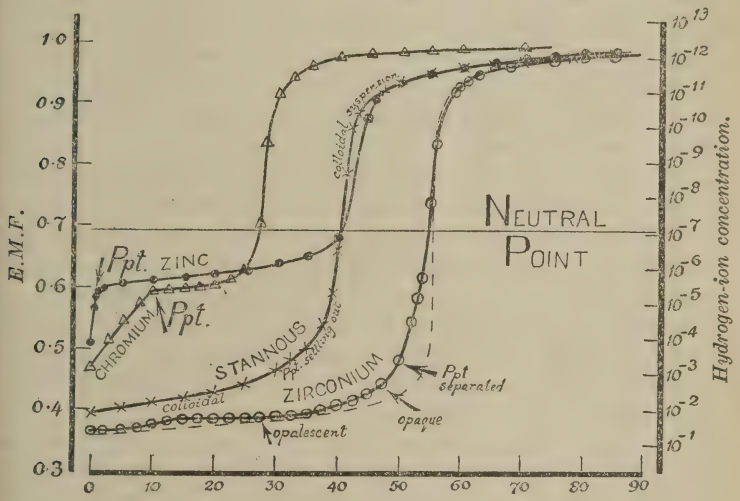
Hydroxides of Zinc, Chromium, Bivalent Tin, and Zirconium.— The titration curves are given in Fig. 2 and the particulars of the solutions in the following table. The temperature was 18°.

Soln. titrated (100 c.c.).	Normality of NaOH.	C.c. of NaOH theoretically required.	Precipitate first appeared. *E.M.F.*	p_H.	C.c. of NaOH.
0·025*M*-$ZnSO_4$	0·090	55·55	0·583	5·20	0·6
0·005*M*-$Cr_2(SO_4)_3,K_2SO_4$ (violet)	0·100	30·0	0·591	5·34	10·0
0·020*M*-$SnCl_2$	0·0932	42·9	—	—	—
0·01*N*-HCl ..... and	0·090	HCl = 11·1	Opalescent at 0·390	1·86	27·5
0·01*M*-$ZrCl_4$	—	Total = 55·5	Ppt. at 0·444	2·79	47·5

The curve representing the precipitation of zinc sulphate with sodium hydroxide shows that a basic sulphate was obtained. Precipitation was complete when 1·53 equivalents of alkali had been added, which may have been due to the separation of a basic sulphate, $ZnSO_4,3ZnO$. Pickering (J., 1907, **91**, 1981), who found that precipitation was complete and the solution had become alkaline to phenolphthalein when 1·59 equivalents of alkali had been added, concluded that the basic sulphate $ZnSO_4,4ZnO$ had been produced. As in other cases, the amount of alkali required was determined by the rate at which it was added, it appearing to be a rule that

the more slowly the alkali is added the less basic is the precipitate; this, once formed, is decomposed slowly by further additions of alkali. This no doubt accounts for the greater amount of alkali required by Pickering. It is almost certain that the precipitate formed does contain at least one definite basic salt, but the evidence at present available is insufficient to establish its individuality. Of the basic sulphates which have been described, that, with varying water contents, suggested by the titration seems to be the one described by the majority of workers, among whom may be mentioned Graham (*Phil. Trans.*, 1837, **127**, 47).

Fig. 2.



Sodium hydroxide began to produce a precipitate from zinc sulphate solution at p_H 5·2. It was shown in Part I that the solubility products of magnesium and manganous hydroxides calculated from the titration curves compare satisfactorily with those given by other methods, in spite of the fact that the precipitates actually obtained are basic. If the method be applied to the zinc titration, a value is obtained which is considerably at variance with the recorded values. Thus the extrapolated *E.M.F.* at 18° = 0·600 volt, therefore $p_H = 5{\cdot}48$, and the extrapolated amount of 0·090*N*-sodium hydroxide = 0·8 c.c., therefore $C_{Zn^{\cdot\cdot}} = 3{\cdot}6 \times 10^{-4}$, and consequently $[Zn^{\cdot\cdot}][OH']^2 = 10^{-21}$ approx. The values so far recorded are those by Herz (*Z. anorg. Chem.*, 1898, **23**, 227) and Bodländer (*Z. physikal. Chem.*, 1898, **27**, 66), who found the solubility of zinc hydroxide to be 2·6 and $2{\cdot}5 \times 10^{-5}$ gram-mol. per

litre respectively, from which the respective solubility products 1·8 and 1·6 $\times$ 10^{-14} are obtained. These values appear to be incorrect, for if correct they would correspond to a hydrogen-ion concentration of about 10^{-9} at which zinc hydroxide would be precipitated, as is the case with manganous hydroxide, whose solubility product is 1·3 $\times$ 10^{-14}. It will be shown in a later paper dealing with the precipitation of basic zinc salts—chromates, carbonates—that such a hydrion concentration could not possibly be correct.

Complete re-solution of the zinc hydroxide did not take place in the course of the titration, although more than two molecules of sodium hydroxide were added in excess of that required to form zinc hydroxide. These measurements give no insight into the acidic nature of zinc hydroxide, no inflexions having appeared when either 83·3 or 111·1 c.c. of alkali, the amounts required to form the zincates having the respective formulæ $NaHZnO_2$ and Na_2ZnO_2, had been added. Calculation, however, shows that the concentration of hydroxyl-ions in the alkaline solutions was slightly less than would have been the case had no substances other than the alkali been present. For example, the p_H of the solution containing the alkali required to form $NaHZnO_2$ was 12·06 as compared with the calculated value 12·25. It is probable that the diminution in hydroxyl-ion concentration was due both to some chemical action and to adsorption having taken place. This view is supported by the conductivity measurements of Chatterji and Dhar (Faraday Soc., "Symposium on Colloids," 1921, p. 123), who state that whereas the conductivity of sodium hydroxide was not appreciably changed by the addition of the majority of amphoteric hydroxides, the change when zinc hydroxide was added was pronounced. Similar observations were made by Carrara and Vespignani (*Gazzetta*, 1900, **30**, 35) with potassium hydroxide solutions of zinc hydroxide. Hildebrand and Bowers (*J. Amer. Chem. Soc.*, 1916, **38**, 785) studied with the hydrogen electrode the reaction of alkalis with certain zinc salts and they claim to have obtained distinct evidence of the existence of monobasic zincic acid, $HHZnO_2$, for they found a sudden increase in p_H at the point where the amount of sodium hydroxide added was that required for the formation of $NaHZnO_2$. Repeated titrations have been made by the author on zinc salt solutions of the concentration used by Hildebrand and Bowers, but hitherto their observation has not been confirmed. It is interesting to recall that since Hildebrand and Bowers's paper appeared Goudriaan (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 179) has investigated the isotherm at 30° of the ternary system Na_2O–ZnO–H_2O and has found that

the only salt of sodium and zinc hydroxides is $Na_2ZnO_2.4H_2O$, which happens to exist in equilibrium with concentrated sodium hydroxide solutions containing from 27·8 to 39·2% of Na_2O. This salt is decomposed by water and so are the liquid phases with which it exists in equilibrium, for on dilution they deposit zinc hydroxide.

Chrome alum was chosen for the titration of the chromium salt, as it dissolves to give the normal violet solution. No precipitate was formed until one-third of the stoicheiometric amount of sodium hydroxide had been added—the p_H having previously rapidly increased until the precipitation p_H had been reached. The amount of alkali required to cause the beginning of precipitation seems to suggest that the basic salt retained in the solution had the formula $Cr(OH)SO_4$. It is probably a coincidence, for dissolved chromium sulphate can be rendered more basic and still remain in solution. The curve shows that the mother-liquor became alkaline when 27·5 c.c. (= 5·5 equivalents) of alkali had been added—an amount pointing to the final composition of the precipitate being $Cr_2O_3,0·25SO_3$. Williamson (*J. Physical Chem.*, 1923, **27**, 384) found, by adding varying amounts of sodium hydroxide to a decimolar solution of chrome alum, that when from 2 to 5 equivalents of alkali are added to one molecule of chrome alum the precipitates are almost constant in composition, $Cr_2O_3,0·7SO_3.3·6H_2O$, but when 6 equivalents are employed the precipitate is still more basic, as shown by the formula $Cr_2O_3,0·28SO_3,3·18H_2O$. This formula is similar to that indicated by the titration. Thus it appears that during the steady increase in p_H occurring while from 10 to 22 c.c. of alkali were being added a basic sulphate of approximately constant composition was being formed, which after precipitation became more hydrolysed by the further addition of alkali.

The titration curve affords no evidence of the constitution of alkaline solutions of chromium hydroxide, although the amount of alkali which was added was in excess of that required to form Na_3CrO_3. The amount of alkali was insufficient to dissolve the chromium hydroxide. The potential differences obtained in the alkaline solutions pointed to hydroxyl-ion concentrations which were a little less than those obtained by calculation. The difference may probably be accounted for by adsorption by the chromium hydroxide or possibly by some little union having taken place. Fricke and Windhausen (*Z. anorg. Chem.*, 1924, **132**, 273) also have shown that there is a slight difference in hydroxyl-ion concentration observable between sodium hydroxide solutions and those of chromium hydroxide in sodium hydroxide of the same concentration when measured by the Hg|HgO electrode.

Electrometric titrations were now carried out on violet and green solutions of chromium salts to see if some clue to the difference of colour could be discovered. The Werner co-ordination theory is generally held to give the most plausible explanation of the violet and green forms. Werner and Gubser (*Ber.*, 1901, **34**, 1579) first applied the theory to chromium chloride, and quite recently Lamb and Fonda (*J. Amer. Chem. Soc.*, 1921, **43**, 1154) referred to its application to chromium salts as " perhaps the most striking exemplification of the Werner theory of molecular structure." It is therefore surprising that the evidence on which Werner and Gubser based their views is quite unconvincing, and indeed, the difference might well be due to the existence in the green solutions of basic aggregates which are essentially colloidal in nature. The low conductivity of solutions of the green form of chromium chloride was regarded as evidence of the dissociation of a binary salt, $(CrCl_2,4H_2O)Cl,2H_2O$. The abnormal molecular weights calculated from the depression of the freezing point were supposed to supply fundamental evidence for this structure of the green form, for they happened to be of the order of one-half the molecular weight of hexahydrated chromium chloride. It is strange that the weight of six molecules of water should have been included in the latter molecular weight, seeing that four molecules only are supposed to be present in the nucleus of the complex chromium kation. The observed molecular weights of the violet chromium chloride were of the order of one-quarter of that of the hexahydrated salt, and this was taken as being due to $(Cr6H_2O)Cl_3$. The results show, however, that the observed molecular weights of the violet chloride in the more dilute solutions are somewhat too high—this may be regarded as due to incomplete ionisation—but it is surprising to find that the agreement between the observed and the theoretical values becomes perfect for a 12% solution, in which the dissociation must be far from complete. Werner and Gubser tried to confirm the view that only one chlorine atom in the green form was ionisable and therefore precipitable with silver nitrate, but always found that the amounts precipitated were greater than that corresponding to one atom, even in rapid estimations carried out at 0°. Similar observations have also been made on the incomplete precipitation with barium chloride from green chromium sulphate solutions. It is difficult to reconcile with the co-ordination theory the observations of Weinland and Koch (*Z. anorg. Chem.*, 1904, **39**, 296) on the precipitability of chlorine from green chromium chloride solutions with various silver salts, both in presence and in absence of free acid. The amount of chlorine precipitated depended on the nature and the quantity of the

particular silver salt used; without the addition of acids, all the silver salts precipitated at least two-thirds of the chloride. The presence of nitric acid had the effect of diminishing the amount of chloride liberated, whereas the silver salts of weak acids, such as acetic, lactic and nitrous, and silver sulphate immediately precipitated all the chloride. Silver salts of strong acids did not cause complete precipitation and free strong acids suppressed the precipitation even more. Lamb (*J. Amer. Chem. Soc.*, 1906, **28**, 1710; Lamb and Fonda, *ibid.*, 1921, **43**, 1154) tried to explain the above observations by a gradual transition from the green variety to the violet due to the hydrogen-ion concentrations ruling during the reactions, but in order to show how the transformation took place they found it necessary to postulate further that the green variety first underwent hydrolysis to form some such basic complex as $CrCl_2OH$.

The essential difference between the violet and the green salts of chromium appears to be concerned with the amount of hydrolysis and with a change in the chromium hydroxide which is probably akin to that produced by ageing. The normal or violet salts must therefore be prepared under such conditions that the hydrolysis is minimised by crystallising at as low a temperature as possible from very strongly acid solutions. The simplest way to convert the violet form into the green is by boiling. By so doing, the hydrolysis becomes enhanced and it is probable that the chromium hydroxide bound in the form of aggregates of basic salt tends to lose its reactivity. The change also seems to be linked up with the treatment to which the chromium hydroxide had been subjected previous to its solution in acids, for, as shown by Recoura (*Compt. rend.*, 1895, **120**, 1337), the change from violet to green can be effected by allowing an alkali solution of chromium hydroxide to age before dissolution in acid. It has been shown that the change in colour of chromium sulphate solutions is accompanied by the liberation of acid (see Denham, *Z. anorg. Chem.*, 1908, **57**, 361—bibliography given) with the consequent separation of a soluble basic salt. The dialysis experiments of van Cleeff (*J. pr. Chem.*, 1881, **23**, 58) and Richards and Bonnet (*Proc. Amer. Arts Sci.*, 1903, **39**, 1) show that the soluble basic aggregates are colloidal in nature, for the residue left in the dialyser from green solutions was basic whereas violet chromium sulphate passed through completely. Again, Richards and Bonnet have shown that in the precipitation of sulphate as barium sulphate from green sulphate solutions green basic chromium sulphate was always carried down.

The fact that barium chloride and silver nitrate produce incomplete precipitation appears to be a property in common with other

elements which give solutions which are almost certainly colloidal. Thus the chloride in ferric oxide hydrosols is not readily precipitated with silver nitrate, neither is it completely precipitated from solutions of either ferric or zirconium chloride in the cold, and especially after the solutions have been allowed to stand or have been boiled.

The change of violet solutions to green immediately on the addition of a little alkali is significant. The green colour of the solution containing the soluble basic chromium salt is undoubtedly connected with the existence of the green chromium hydroxide in solution in the form of basic aggregates.

Hydrogen electrode titrations have been carried out at 18° of violet solutions of both the chloride and the sulphate, and also of green solutions which were prepared by boiling the normal solutions for 5 minutes and rapidly cooling to 18°. The initial readings are given in the following table.

Salt.	Conc.	Colour.	*E.M.F.* against *N*-calomel.	p_H.	% Hydrolysis.
Chloride.....	0·0133	Blue	0·467	3·19	1·62
	0·0133	Green	0·409	2·18	16·4
Sulphate.....	0·0050	Violet	0·467	3·19	2·16
(as chrome alum)	0·0067	Green	0·395	1·94	28·7

The percentage of hydrolysis has been referred to the total amount of combined acid. It will be seen that the effect of boiling for a short time was to increase the amount of hydrolysis more than tenfold. The titration curves are similar to that given by chromium sulphate (Fig. 2), with the exception that the sections prior to precipitation in the case of the green solutions are somewhat curved, owing to the neutralisation of the liberated acid, instead of being rectilinear as in the case of the violet or blue solutions. The following table gives the important features of these titrations.

	Precipitation began.			Precipitation complete.
Salt.	*E.M.F.*	p_H.	Equivs. of NaOH to 1 equiv. of Cr.	Equivs. of NaOH.
Blue $CrCl_3$	0·588	5·28	1·07	2·78
Green $CrCl_3$	0·586	5·25	1·43	2·85
Violet chrome alum	0·591	5·30	1·00	2·75
Green chrome alum	0·587	5·27	1·21	2·71

The table shows that in each case precipitation was dependent on the attainment of a hydrion concentration, p_H 5·3, and that precipitation began from those solutions which contained chromium in the normal condition when about one equivalent of sodium hydroxide had been added, whilst the green solutions did not yield precipitates until somewhat larger proportions of alkali had

been added. The greater amounts of alkali required in the latter case show that the change produced in the solutions on turning from violet or blue to green has rendered the chromium salts more resistant in their behaviour towards alkali.

It is probable that the basic chromium complexes which seem to be present in green solutions are "micellar" in structure and constitute a colloidal electrolyte in which the kations are composed of chromium hydroxide and varying amounts of acid radical, a portion only being ionisable, and may perhaps be represented thus:

$$\left[\begin{matrix} & (OH)_{3x} \\ Cr_{(x+y+1)} & \\ & R_{3y} \end{matrix}\right] R_3 \rightleftharpoons \left[\begin{matrix} & (OH)_{3x} \\ Cr_{(x+y+1)} & \\ & R_{3y} \end{matrix}\right]^{\cdots} + 3R',$$

x and y being indefinite. Some such arrangement as this would account for the slowness with which silver chloride and barium sulphate may be precipitated from the appropriate green solutions, and this is especially so when the chromium solutions happen to be basic, such as may be prepared from the basic glassy masses obtained by evaporating solutions of chromium salts to dryness. There appears to be a tendency for one-third of the combined acid in a chromium salt, *i.e.*, the amount corresponding to that which seems to be loosely combined and gives rise to the formation of the "soluble basic salt," to be driven off on evaporation. Thus a basic salt prepared in this way had a composition corresponding to $Cr(OH)SO_4$ and gave in solution no precipitate with barium chloride; neither did it do so with ammonia except on boiling or keeping. The soluble basic complexes in the green solutions have some properties in common with chromium hydroxide. Chromium hydroxide which has been suspended in water and boiled, or has been allowed to stand, becomes difficultly soluble in acids, as is also the case with ferric hydroxide, slowly dissolving only in concentrated acid solutions. Hence it is evident why the acids present in Weinland and Koch's experiments did not immediately decompose the green salt and render the chloride available for precipitation, and why the acid actually retarded the precipitation by depressing the ionisation of the colloidal electrolyte. The conception of basic aggregates also supplies an explanation why it was only the silver salts of weak acids which caused nearly all the silver chloride to be precipitated. The first reaction taking place between the precipitant and the colloidal electrolyte is one of double decomposition, whereby the chloride anion of the chromium complex is replaced by the anion of a weak acid. This would diminish the hydrogen-ion concentration of the solution, which would therefore tend to approach the value requisite for the precipitation of

chromium hydroxide; the basic complexes would thus be rendered so unstable that the chloride radicals in them would become susceptible to reaction with the silver salt.

A qualitative comparison of the absorption spectra of solutions of equal concentrations of (*a*) violet chrome alum, (*b*) green chrome alum, and (*c*) violet chrome alum to which an excess of sodium hydroxide had been added, revealed that those of solutions (*b*) and (*c*) were similar. The main difference between (*a*) and (*b*) was that the very faint yellow band, 5750—5950 Å., in the former had become wider and more pronounced in the latter, 5660—6110 Å. There was also some absorption in (*b*) in the blue region extending up to 4840 Å.; that in (*a*) extended to 4530 Å. The spectra of (*b*) and (*c*) were identical over the short wave-lengths, but the yellow band was found to have moved a little, to 5800—6160 Å. It is probable that alkaline solutions of chromium hydroxide are largely colloidal, and the similarity of the last two spectra would suggest that some part of the green solution also was colloidal, in which case the increased absorption might be attributed to the presence of exceedingly small colloidal basic aggregates.

The stannous chloride solution used in the titration shown in Fig. 2 was turbid and became more and more so until 30 c.c. of alkali had been added, when a heavy precipitate began to settle; the precipitate passed back again into colloidal suspension as soon as the solution had become alkaline ($p_H = 8{\cdot}7$) and 41·0 c.c. of sodium hydroxide had been added. From the *E.M.F.* readings made during the titration, the amounts of hydrolysed hydrochloric acid have been calculated at the various stages, from which the compositions of the basic stannous chloride aggregates given in the following table have been calculated.

C.c. of 0·0932*N*-NaOH.	*E.M.F.*	Atoms of Cl neutralised.	Fraction of unneutralised HCl hydrolysed.	Comp. of basic stannous chloride. To 1 atom of Sn.		Mol. of HCl hydrolysed.
				Cl.	OH.	
0	0·391	0	0·336	1·33	0·67	0·67
5·1	0·401	0·24	0·269	1·29	0·71	0·47
10·0	0·412	0·47	0·208	1·22	0·78	0·32
15·2	0·418	0·71	0·204	1·03	0·97	0·26
20·0	0·428	0·93	0·173	0·88	1·12	0·18
25·15	0·440	1·18	0·145	0·63	1·37	0·12
30·0	0·463	1·40	0·085	0·55	1·45	0·05
35·0	0·499	1·63	0·033	0·36	1·64	0·01
39·0	0·585	1·82	0·002	0·18	1·82	0·0004

The table shows that the basic stannous chloride particles varied in composition from $SnCl_{1\cdot33}(OH)_{0\cdot67}$ to $SnCl_{0\cdot55}(OH)_{1\cdot45}$ during the addition of the 30 c.c. of alkali and yet remained in colloidal suspension. The last column indicates that the molecular proportion

of hydrochloric acid hydrolysed gradually grew less as the titration proceeded. It was not until the particles had become to this extent basic, and the concentration of the free hydrochloric acid with which they had existed in equilibrium had become relatively small, that the colloidal solution coagulated. The solution became neutral when 40 c.c. of alkali had been added, showing that chloride was still being retained by the stannous hydroxide, its composition having then become $SnCl_{0\cdot14}(OH)_{1\cdot86}$. The fact that peptisation of the precipitate took place immediately the mother-liquor became alkaline seems to be important, and it may be that the reaction of the alkali with the retained chloride in the precipitate was largely responsible. No inflexion was produced in the curve in the alkaline zone.

Hildebrand (*loc. cit.*), besides finding an inflexion for zinc hydroxide, found one for zirconium hydroxide also. The precipitation of zirconia from a solution in hydrochloric acid has been investigated (Fig. 2) and also the change in p_H in the mother-liquor when the precipitated zirconium hydroxide was in presence of an excess of sodium hydroxide. The present experiments fail to confirm Hildebrand's observation of a distinct inflexion, which he stated to correspond to the formation of sodium zirconate. There appear to be absolutely no grounds for regarding zirconium hydroxide as amphoteric. Unlike the other hydroxides studied in this paper, that of zirconium is not dissolved by alkalis under any conditions. In common with all other gelatinous hydroxides, it adsorbs salts from solutions in which it may be suspended, and on precipitation with an excess of alkali does naturally adsorb some alkali, the amount depending on the quantity of alkali present. These precipitates do not hold the alkali in any form of combination, as would be the case if they contained insoluble zirconates. It is remarkable that whilst alumina is one of the few oxides which can be considered with any degree of certainty to be amphoteric in the wet state, it should be the only one which is definitely amphoteric in the dry state, yielding on fusion with alkalis or with alkali metal carbonates products which are soluble.

The titration curve gives some insight into the mechanism of precipitation. The hydrochloric acid solution was prepared from a basic zirconium chloride which contained 1·737 mols. of Cl to 1 mol. of ZrO_2. The basic chloride dissolved in water to give a perfectly clear solution. An aqueous solution, 0·04 normal with respect to the chloride content, was hydrolysed immediately after preparation to the extent of 54%. The dotted line in the diagram represents the neutralisation curve of hydrochloric acid solution having the same chloride concentration as that of the acid solution

of zirconium chloride with the same alkali solution. The small but definite inflexion which occurred when 11·1 c.c. of alkali had been added is remarkable. It marks the end of the neutralisation of the excess of acid over that required to form zirconium tetrachloride and thus points to the existence in solution of zirconium chloride, although considerably hydrolysed. This is opposed to the generally accepted view that the chloride dissolves as "zirconyl chloride," $ZrOCl_2$, dissociating into "zirconyl" ions, $ZrO^{\cdot\cdot}$, and Cl', and free hydrochloric acid. The solution began to become opalescent when 27·5 c.c. of alkali had been added, and this was before the amount of alkali had been added which was necessary to form either $ZrOCl_2$ (33·3 c.c.) or the basic salt from which the solution was prepared (36·2 c.c.). As solutions of both these substances happen to be perfectly clear, it follows that the premature opalescence obtained in the titration must have been due either to the electrolytes present or to the hastened growth of the colloidal particles owing to the rate at which the alkali was added. It must have been due to the latter, for salts may be added to basic zirconium chloride solutions of similar composition without producing any perceptible effect. The zirconium chloride curve tends to approach the hydrochloric acid curve when approximately two equivalents of sodium hydroxide have been added (33·3 c.c.). At this stage the chloride radicals in combination with the zirconium were undergoing the maximum hydrolysis. The solution became increasingly colloidal in appearance as the alkali was added until it became opaque and coagulation suddenly took place (47·5 c.c.). The following table gives the fraction which had suffered hydrolysis of the portions of zirconium chloride which had not entered into the reaction at the various stages in the titration, from which has been found the composition of the unhydrolysed basic zirconium chloride together with the molar proportion of the free acid which had been hydrolysed.

C.c. of NaOH.	*E.M.F.*	Atoms of Cl neutralised.	Fraction of unneutralised HCl hydrolysed.	Comp. of basic chloride. To 1 atom of Zr. Cl.	Comp. of basic chloride. To 1 atom of Zr. OH.	Mols. of HCl hydrolysed.	Remarks.
0	0·366	0	0·529	2·12	1·88	3·12	Free HCl
11·1	0·380	0	0·579	2·32	1·68	2·38	,,
22·2	0·386	1·0	0·670	3·01	0·99	2·01	Clear
27·8	0·390	1·5	0·714	3·28	0·72	1·78	Opalescent
33·3	0·393	2·0	0·828	3·66	0·34	1·66	,,
36·2	0·397	2·267	0·831	3·70	0·30	1·44	,,
38·9	0·406	2·5	0·685	3·53	0·47	1·03	,,
44·4	0·426	3·0	0·480	3·48	0·52	0·48	,,
47·5	0·444	3·28	0·333	3·52	0·48	0·24	Opaque
50·0	0·481	3·5	0·107	3·55	0·45	0·05	Coagulated
52·7	0·571	3·75	0·006	3·75	0·25	0·00	,,

In these calculations it has been assumed that the hydrochloric acid was completely dissociated. The degree of hydrolysis of the zirconium chloride in the free acid solution was obtained by subtracting the hydrion concentration produced by the excess of acid from the total hydrion concentration calculated from the observed voltage.

It will be seen that the maximum hydrolysis occurred when just over two atoms of chloride of the zirconium chloride had been reacted upon, and that the rapid increase in hydrolysis during the first portion of the titration was accompanied by a corresponding change in the composition of the basic zirconium chloride actually present in the solution (columns 5 and 6). Thereafter, the composition of the basic zirconium chloride remained nearly constant and corresponded roughly with the formula $Zr(OH)_{3\cdot5}Cl_{0\cdot5}$, until after coagulation ensued, when it was partially decomposed by the alkali. The first half of the titration, besides yielding a rapidly increasing basic chloride, was accompanied by a gradual decrease in the amount of free acid, which tended to render the basic zirconium chloride more and more insoluble and thus produced a gradual growth in the size of the basic chloride particles. At the beginning of the titration the particles probably approximated to molecular dimensions, but as the chloride became more and more basic these exceedingly small particles coalesced to form larger and larger aggregates until they became sufficiently big to render the solution opalescent, and this process still continued through the period when the solution had become visibly and increasingly colloidal right up to the point when coagulation occurred. The table shows that the free acid had some inhibiting effect on this growth in the size of the particles, for it was only after an appreciable proportion of the acid had been neutralised that the solution became opalescent, and, after the basic chloride particles had become uniform in composition, it was only after the amount of free acid had been almost removed that the colloidal solution coagulated.

These observations seem to suggest that the nature of basic zirconium salt solutions is essentially colloidal in spite of the fact that many of the solutions are perfectly clear. Müller (*Z. anorg. Chem.*, 1907, **52**, 316) arrived at the same conclusion from a study of the reactions of zirconium salt solutions. The observations, moreover, furnish an excellent example to show that the process of precipitation is one which involves the formation of a colloidal solution which subsequently coagulates. In the majority of precipitations the colloidal solution stage is so rapidly passed that it is not observed.

Adolf and Pauli (*Kolloid Z.*, 1921, **29**, 173) found that the hydrolysis of solutions of zirconium oxychloride, $ZrOCl_2$, of concentrations ranging from 0·0022 to 0·125*M*, after 10 days' standing, varied irregularly between 35 and 50%. As mentioned above, a freshly prepared solution of zirconium chloride containing 1Zr : 1·737Cl was hydrolysed to the extent of 54%, whereas in the solution containing the basic chloride having the same composition in the titration the hydrolysis was considerably greater, *viz.*, 83·1%. In the latter case, the solution was opalescent and therefore contained larger particles than the corresponding clear solution. Thus the degree of hydrolysis appears to be a function of the size of particle, and consequently the smaller amount of hydrolysis in the clear solutions of Adolf and Pauli must have been due to the presence of particles which had been rendered small by the solution effect of the free acid. They prepared zirconium oxide hydrosols by dialysis, which contained appreciable amounts of chloride; one contained 0·33 atom of chlorine and the other 0·26 atom to each atom of zirconium. Both sols were hydrolysed to small extents, *viz.*, 0·9 and 0·6%. It is important to note that, although the concentration of free acid was small, there was a relatively large concentration of chloride ions, 41 and 37% respectively of the total chlorine content. The ratio Zr : Cl in these hydrosols corresponds to points on the titration curve lying between those representing 3·5 and 3·75 equivalents of sodium hydroxide, *i.e.*, just after coagulation had taken place. The amount of free acid was of the same order in both the colloidal solutions and the mother-liquor in which the basic zirconium precipitate was suspended. The large concentration of chloride ions in the colloidal solutions shows that the basic chloride particles do dissociate in some way.

The degree of dispersion of colloidal basic chloride solutions appears to be dependent on the amount of acid present. Colloidal solutions of basic chloride in which some free acid is present tend to become clear on standing, no doubt owing to the tendency of the colloidal particles to pass into solution. This behaviour may possibly account for Rodd's observation (J., 1917, **111**, 396) that a basic chloride, $Zr_5O_8Cl_4,22H_2O$, separated at first from concentrated solutions of zirconia in which the concentration of hydrochloric acid had been suitably regulated. When the solution had become more acid owing to separation of the highly basic chloride, crystals of ordinary $ZrOCl_2,8H_2O$ began to separate. Rodd believed that the formation of the very basic chloride (Zr : Cl = 5 : 4) was due to some intrinsic change having taken place in the constitution of the zirconium hydroxide. The important point is

that the salt appears to have given a clear solution, whereas when the zirconium chloride present in the solution undergoing titration had acquired the same composition by the addition of 35·5 c.c. (= 3·2 equivalents) of sodium hydroxide the solution became opaque. Rodd mentions that a solution of his salt was precipitated by either sulphuric acid or sulphates generally. There seems to be no doubt that Rodd obtained his highly basic chloride through using a concentration of hydrochloric acid much less than that required for the crystallisation of the usual $ZrOCl_2,8H_2O$, and thus obtained a substance nearly as basic as that shown to exist in the solution during the second part of the titration, *viz.*, $Zr(OH)_{3\cdot5}Cl_{0\cdot5}$. Rodd's salt is $Zr(OH)_{3\cdot2}Cl_{0\cdot8}$. The fact that Rodd obtained his salt by a slow crystallisation process from an acid solution indicates that it must have been composed of very small particles, their growth having been prevented by the acid present. Hence the reason for the substance passing into a clear or nearly clear solution. The fact that sulphates in general caused its precipitation appears to be an example of the normal behaviour of electrolytes towards colloidal solutions. Rodd, however, believed these precipitations to be cases of double decomposition, as the precipitates obtained by the addition of sulphuric acid and ammonium sulphate were within a few units % of the same composition, $Zr_5O_8(SO_4)_2,14H_2O$. He was of the opinion that this formula represents a " true chemical individual," but added that there was " no evidence to show that this is a true hydrate."

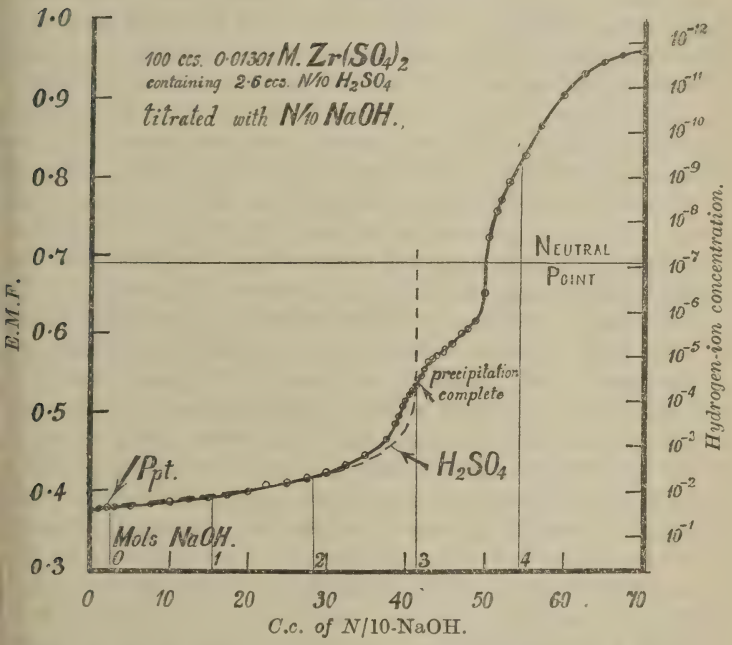
Solutions of zirconium sulphate behave towards some reagents in a manner quite different from that of solutions of either the chloride or the nitrate, so much so that Ruer (*Z. anorg. Chem.*, 1904, **42**, 85) and others have postulated that the sulphate must exist in solution as a complex zirconium sulphuric acid in which the zirconium is present in a complex anion and thereby escapes precipitation. Thus oxalic acid and alkali metal oxalates fail to precipitate it, and sulphites only precipitate it slowly and incompletely. If potassium chloride be added to a zirconium sulphate solution, either before or after the addition of sodium oxalate, the solution becomes readily precipitable. Another point of difference is the behaviour towards sodium tartrate. Zirconium chloride yields a precipitate with sodium tartrate, readily soluble in excess, as compared with the precipitate which is obtained from zirconium sulphate solution, which dissolves only on boiling or on prolonged standing. The precipitate in the latter case is mainly basic zirconium sulphate. Chauvenet (*Ann. Chim. Phys.*, 1920, **13**, 82) titrated several zirconium salt solutions conductimetrically and found that the titration curves, instead of being straight lines as

in acid–alkali neutralisations, were slightly curved, such that the tangents drawn to the curves at each end intersected at points corresponding to approximately two equivalents of alkali. This he claimed to be evidence for the existence of the "zirconyl," $ZrO^{\cdot\cdot}$, radical. The data given in the previous table show that during the addition of the first two equivalents of alkali the basic chloride undergoes hydrolysis and the remaining two equivalents cause little variation in its composition, $Zr(OH)_{3\cdot5}Cl_{0\cdot5}$, except at the end. These two processes, which took place in the precipitation from zirconium chloride solution, undoubtedly account for the change in the slope of Chauvenet's curve, which had therefore nothing to do with an alleged zirconyl radical. Chauvenet also titrated a solution of zirconium sulphate by the conductivity method and obtained the point of minimum conductivity when 3 equivalents of alkali had been added; this he claimed to be due to the separation of a definite basic sulphate, $ZrOSO_4,ZrO_2$. He also claimed that an inflexion was produced when two equivalents of alkali had been added, which pointed to another definite basic salt, zirconyl sulphate, $ZrOSO_4$. In view of the peculiar properties shown by zirconium sulphate and of the contentions of Chauvenet, it was decided to subject the sulphate to titration with the hydrogen electrode.

The zirconium sulphate had the composition $ZrO_2,2{\cdot}10SO_3,2{\cdot}29H_2O$, from which a $0{\cdot}01301M$-$Zr(SO_4)_2$ solution was prepared at room temperature; therefore 100 c.c. of the solution contained uncombined sulphuric acid equivalent to 2·56 c.c. of N/10-alkali. The curve showing the titration with N/10-sodium hydroxide of 100 c.c. of this solution at 18° is given in Fig. 3. The first inflexion occurred when the added alkali was equivalent to 3 mols. to 1 mol. of zirconium sulphate. At this point precipitation was complete and the solid had the composition $ZrO_2,\frac{1}{2}SO_3,xH_2O$. Further addition of alkali (up to 50·4 c.c.) caused its partial decomposition and the mother-liquor became alkaline. The precipitate must then have contained $ZrO_2,0{\cdot}16SO_3$, but, as the slope of the curve shows, during the addition of the next few c.c. of alkali some alkali was still being withdrawn from the solution and utilised in decomposing the precipitate still more. The sulphate solution, unlike that of the chloride, began to yield a precipitate immediately the alkali was added. It is curious that by warming zirconium sulphate solution it may be made strongly basic by means of alkali without the separation of a precipitate, the solution remaining quite clear. The dotted curve given in Fig. 3 is the titration curve of 100 c.c. of sulphuric acid containing 41·6 c.c. of N/10-sulphuric acid, equivalent in concentration to three-quarters of the com-

bined acid in the zirconium sulphate solution together with the small amount of free sulphuric acid. The two curves are nearly coincident over the first half of the zirconium sulphate curve, but vary a little during the addition of the third equivalent. The curves show therefore that the zirconium sulphate solution contained a basic sulphate and free sulphuric acid in approximately the proportions 1 mol. of $ZrO_2,\frac{1}{2}SO_3$ to $1\frac{1}{2}$ mols. of H_2SO_4. The addition of alkali had the main effect of neutralising the free sulphuric acid, with the consequence that the basic sulphate with which it had existed

FIG. 3.



some kind of equilibrium was precipitated. The curves give no evidence of Chauvenet's so-called zirconyl sulphate, but do confirm his observation of the precipitation of a basic sulphate of approximately the composition $ZrO_2,\frac{1}{2}SO_3$. Further work, however, is necessary on the lines of the phase rule before its individuality can be established.

Chauvenet (*loc. cit.*) determined the molecular weight of zirconium sulphate from the depression of the freezing point of an aqueous solution, and found it to be a little more than a quarter of that of $ZrOSO_4,H_2SO_4$. He therefore argued that zirconium sulphate on solution split up into zirconyl sulphate and sulphuric

acid. If, however, the partial dissociation of sulphuric acid be taken into consideration, the anomalous freezing point might also be taken to support the constitution of zirconium sulphate solution suggested by the above titrations.

The view that these somewhat inert basic zirconium sulphate particles exist in solution in equilibrium with hydrolysed sulphuric acid gives an explanation of the abnormal behaviour of reagents towards zirconium sulphate solutions, especially that of sodium tartrate in precipitating the basic sulphate in such a state that it is not readily soluble in excess of the reagent.

Some criticism appears to be not out of place here of Chauvenet's density method (*Compt. rend.*, 1917, **164**, 864), by which he claimed to ascertain which of the many reported basic zirconium sulphates were definite individuals. He treated zirconia with various quantities of sulphuric acid and dried the products by evaporation at 200°. He stated that at this temperature the products became rigorously anhydrous. Van Bemmelen (*Z. anorg. Chem.*, 1906, **49**, 125) showed that zirconia, when dried at 200°, retained much water which was not completely driven off at 300°. The present author found that after several hours' drying at 200° water was retained to the extent shown by the formula $ZrO_2,0{\cdot}48H_2O$. The salt was found by immersion in nitrobenzene to have the density 4·02, but when rendered water-free by ignition its density was 5·47 (compare 5·489, Venable and Belden, *J. Amer. Chem. Soc.*, 1898, **20**, 273). Zirconium sulphate also requires a much higher temperature than 200° for complete dehydration. By plotting the ratio $ZrO_2 : SO_3$ against the densities, determined by immersion in nitrobenzene, he obtained a curve which had several angular points indicating definite basic salts. On plotting the curve, however, the present author found that all the points lay either on or close to a continuous curve; the small deviations from the curve could readily be accounted for by the considerable experimental errors which the method involved. The determination of the densities of amorphous substances, such as these basic sulphates, is a difficult problem, and the values at best can only be approximate on account of the difficulty of completely filling the porous particles with nitrobenzene. It is conceivable that Chauvenet's density method might be applied in cases where the densities, supposing they could be determined with sufficient accuracy, of the different basic salts were widely different. There is no agreement between Chauvenet's density of $3ZrO_2,4SO_3$, 3·02, and that, 4·1, of Hauser and Herzfeld (*Z. anorg. Chem.*, 1910, **67**, 369). It thus appears that the conclusions of Chauvenet are without satisfactory grounds.

Summary.

(1) The hydrogen-ion concentrations ruling throughout the precipitation of the hydroxides, actually basic salts, of aluminium, beryllium, zinc, chromium, stannous tin, and zirconium have been investigated.

(2) The hydrogen-ion concentrations to be attained for the precipitation of the hydroxides of aluminium, beryllium, zinc, and chromium have been found.

(3) New light has been thrown on the nature of the characteristic soluble basic salt solutions of beryllium, chromium, and zirconium.

(4) The manner of precipitation of stannous and zirconium hydroxides has been shown to be that of the formation and subsequent coagulation of a colloidal solution of dispersed basic chloride particles.

(5) It has been shown that of the bases studied in this paper aluminium hydroxide is the only one which is definitely amphoteric. No confirmation of the observations of Hildebrand on zirconium and zinc hydroxides could be obtained.

(6) The study of zirconium chloride and sulphate solutions has revealed that both are composed of highly dispersed basic particles and hydrolysed acid. No evidence could be obtained of the existence of the " zirconyl " radical.

(7) The hydrogen-ion concentration of precipitation of zinc hydroxide (actually basic sulphate) has been shown to be not in accord with the recorded solubility product data.

(8) It has been shown that the Werner co-ordination theory does not give a satisfactory explanation of the anomalous behaviour of green chromium chloride and sulphate solutions.

In conclusion, the author takes this opportunity to thank Prof. J. C. Philip, F.R.S., for facilities in carrying out this work, the Chemical Society for a grant for the purchase of salts of the rarer metals, and the Department of Scientific and Industrial Research for a personal grant.

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CCLXXXIX.—*Electrometric Studies of the Precipitation of Hydroxides. Part III. Precipitation in the Cerite Group of Rare Earths and of Yttrium Hydroxide by Use of the Hydrogen Electrode.*

By Hubert Thomas Stanley Britton.

The precipitation of the hydroxides of the metals of the "cerite" group and of yttrium has been investigated by means of titrations with the hydrogen electrode. The solutions used and the hydrogen-ion concentrations at which the various precipitations began are given in the table.

Titration and curve No.	Temp.	Solution titrated (100 c.c.).	Normality of NaOH.	Theor. amount of NaOH. (C.c.).	Precipitation began.		
					E.M.F.	p_H.	C.c. of NaOH.
1	17°	0·0133*M*-$La(NO_3)_3$	0·090	44·4	0·763	8·35	1·0
2	17	0·0133*M*-$CeCl_3$	0·1018	39·0	0·709	7·41	1·8
3	17	(1) 0·0163*N*-HCl	0·1018	16·0			
		(2) 0·0114*M*-$PrCl_3$		33·6	0·690	7·05	18·2
4*a*	17	0·0133*M*-$Nd(NO_3)_3$	0·1018	39·0	0·686	7·00	0·8
4*b*	17	(1) 0·0154*N*-HCl	0·1018	15·1			
		(2) 0·0114*M*-$NdCl_3$		33·6	0·687	7·02	18·0
5	18	0·0133*M*-YCl_3	0·090	44·4	0·674	6·78	1·0
6	18	(1) 0·0140*N*-HCl	0·1018	13·75			
		(2) 0·0121*M*-$SaCl_3$		35·53	0·676	6·83	16·1

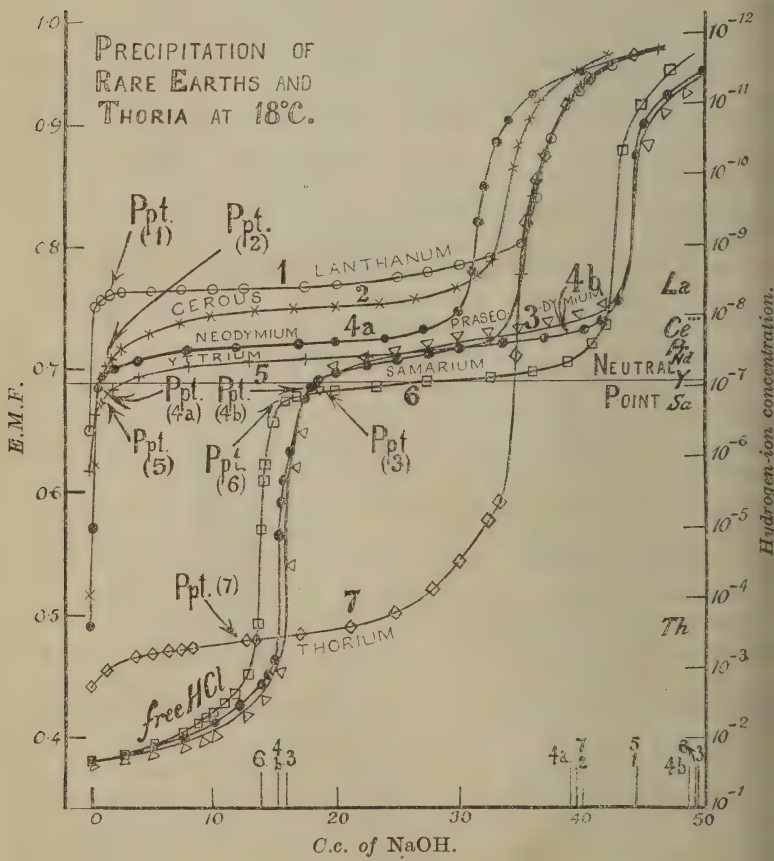
The titration curves are given in the diagram. As thoria occurs with the rare earths in monazite sand, the titration curve (No. 7) of 100 c.c. of 0·01*M*-thorium chloride solution with 0·1016*N*-sodium hydroxide has been included in order that the precipitation p_H of thoria might be compared with those of the rare earths. The great difference in the hydrogen-ion concentrations accounts for the ease with which thoria can be separated from the rare earths of the "cerite" group by those methods which depend on the change in p_H. Knowing the respective hydrion concentrations it is possible to effect the separation of thorium hydroxide from the rare earths by carefully varying the p_H of the solution by means of alkalis and suitable indicators. The hydrogen-ion concentrations may be varied: (*a*) by using reagents which impart hydrion concentrations to the solutions greater than those to be attained for the precipitation

of the rare earths but less than that for thorium hydroxide, and (*b*) by fractional precipitation with bases which produce p_H's which are greater than those produced by the bases to be separated. Methods employing the former device need no control, but those based on the latter principle must be controlled, either as regards the hydrion concentrations by means of indicators or electrometric measurements, or as regards the fractions themselves by determining their chemical equivalents; which is the method usually adopted. The reagents which may be used to control automatically the hydrogen-ion concentrations required in the separation process are: zinc oxide, copper oxide, certain very weak organic bases, and salts of certain acids, such as sodium thiosulphate, and sodium azide if in presence of an excess of hydrazoic acid. Zinc hydroxide (see Part II) and copper hydroxide (see Part IV) are precipitated at a hydrogen-ion concentration of about 10^{-6}. These hydroxides will thus set up in the solution a hydrogen-ion concentration which is less than that required for the precipitation of thorium hydroxide, *viz.* $10^{-3\cdot6}$, but is insufficiently small to cause the separation of the rare earths. Separations by means of weak organic bases such as quinoline and *p*-toluidine have been studied more or less empirically by Jefferson (*J. Amer. Chem. Soc.*, 1902, **24**, 540), Allen (*ibid.*, 1903, **25**, 421), and Hartwell (*ibid.*, p. 1128). In the fractional precipitation with strong bases and oxides such as magnesium and mercuric oxides (see Parts I and IV) the fractionation is much quicker and requires careful regulation. The attainment of too high p_H's at the point where the precipitant impinges on the solution must be avoided, as this may cause the precipitation of undesired hydroxides, which redissolve very slowly.

The hydrogen-ion concentrations which were necessary for the precipitation of lanthanum and cerous hydroxides (curves 1 and 2) were appreciably less than those required for the other four earths. The differences in p_H at which the earths praseodymia, neodymia, yttria, and samaria were precipitated, although very small in the case of the first three, were sufficient to indicate that these are precipitated in the order given, which happens to be the order usually claimed. The closeness of the hydrion concentrations prevailing throughout the precipitations of the hydroxides of praseodymium, neodymium, and yttrium shows that a separation of these three earths by a hydrogen-ion concentration method is impracticable. The strongest base of the yttrium group is generally stated to be yttria, and according to these measurements, it appears to have a strength of the order of that of "didymia." Curves 4*a* and 4*b*, illustrating the respective titrations of the nitrate and chloride of neodymium, show, contrary to the observations of Hildebrand

(*J. Amer. Chem. Soc.*, 1913, **35**, 847), that the hydrogen-ion concentration required for the precipitation of neodymium hydroxide is quite independent of the nature of the anion. Hildebrand found that the p_H value required for precipitation from a chloride solution lay between 7 and 8, but from a nitrate solution between 4 and 5. The lower value obtained for the nitrate solution must have been

FIG. 1.



due to the use of an electrode whose hydrogen was catalytically reducing the nitrate. It has always been found, however, that when such reduction was taking place the *E.M.F.*'s were far from stationary.

In none of these titrations was the pure hydroxide obtained, as is shown by the following amounts (equivalents) of alkali which caused complete precipitation: from lanthanum nitrate solution,

·60; cerous chloride, 2·61; praseodymium chloride, 2·45; neo-
ymium nitrate, 2·38; neodymium chloride, 2·53; yttrium chloride,
·36; and samarium chloride, 2·48.

The separation of basic lanthanum nitrate is yet another example
n which the course of precipitation can be followed through the
ransitional colloidal stage. On the addition of 1·6 c.c. of sodium
ydroxide the solution became opalescent. During the addition
f the first 35 c.c. of alkali (=2·37 equivalents) there was a gradual
ncrease in p_H from 8·35 to 9·0, which did not cause the separation
f a precipitate, for the lanthana passed continuously into the
olloidal state, shown by an increasing turbidity of the solution.
he next 2·5 c.c. caused a rapid diminution in the hydrion concen-
ation, which was accompanied by a rapid increase in turbidity,
hilst the next c.c. caused the solution first to become opaque
nd then to coagulate completely. The hydrion concentration
ad then become $10^{-10·9}$, a value considerably less than that required
r the precipitation of lanthana. The amount of alkali required
nows that the composition of the precipitate was given by
$a(OH)_{2·6}(NO_3)_{0·4}$, indicating, as in other instances, that the
ispersed particles were basic. The sudden fall in the hydrion
oncentration towards the end of the reaction was caused by an
xcess of alkali having passed into the mother-liquor, and must have
een due to the action of this alkali on the colloidal particles which
timately brought about the coagulation of the colloidal solution.

If the order of the precipitation of the hydroxides is actually
at of their basic strengths, the basic strengths of the rare earths here
vestigated lie between those of zinc and manganous hydroxides,
nd below that of magnesium hydroxide. Lanthanum hydroxide
always stated to be the strongest base of the rare earths, and the
cerite " group of hydroxides, excepting ceric hydroxide, to be the
oup of the strongest bases. Apart from lanthanum hydroxide
nd perhaps cerous hydroxide, the other earths appear to be quite
oderate in strength and are comparable with cobalt and nickel
ydroxides. This is contrary to the view generally held. Friend
Text Book of Inorganic Chemistry," 1917, Vol. IV, p. 257)
ates that " from general chemical and thermochemical consider-
ions it may be concluded that they [the rare earths] are stronger
an magnesia, but weaker than the alkaline earths." The chemical
nsiderations are epitomised thus : " The strongly ignited oxides
e readily soluble in mineral acids, several of them combine directly
ith water and absorb carbon dioxide from the air, and all of them
erate ammonia from cold solutions of ammonium salts. Normal
lts of numerous weak acids, *e.g.*, chromic, carbonic, are readily
epared." If the hydrogen-ion concentration relationships do

give the true order of basic strengths, then zinc hydroxide is a weaker base than either of the tribasic hydroxides of the " cerite " elements; yet its oxide after ignition is readily soluble in mineral acids. The behaviour of the rare earths towards cold ammonium salt solutions is misleading. The fact that a base forms well-defined salts with weak acids probably offers no clue to its strength, if those salts happen to be almost insoluble. This is the case with the carbonates and chromates of the rare earths (*vide* Britton, J., 1924, **125**, 1875). Thus thorium hydroxide is an exceedingly weak base, but under certain conditions it forms an extremely well-defined chromate; under other conditions it behaves like other weak bases and gives precipitates which are indefinite and basic (*vide* Britton, J., 1923, **123**, 1429). The power to form well-defined salts with weak acids seems to be a property inherent in an element in conferring a small solubility on a salt and probably has nothing whatsoever to do with its power to form a strong base. There is no marked difference in the stability of soluble acetates and that of the acetates of the metals whose hydroxides are precipitated at comparable hydrogen-ion concentrations, *e.g.*, zinc, cobalt, nickel, and cadmium.

Vesterberg found (*Svensk. Kemi Tidskrift*, 1917, **29**, 101 ; *Zeitsch. anorg. Chem.*, 1917, **99**, 11, 22) that equally concentrated solutions of lanthanum acetate and ammonium acetate were equally hydrolysed. This led him to conclude hat the strengths of lanthanum hydroxide and ammonium hydroxide are nearly the same. The titration shows that lanthana was precipitated from an alkaline solution the hydrogen-ion concentration of which varied from $10^{-8\cdot35}$ to 10^{-9}. The very small concentration of lanthanum hydroxide therefore imparts to the solution a hydroxyl-ion concentration of the order of 10^{-5}, a concentration which is restricted by the small solubility of the lanthana. The actual amount of dissolved lanthanum hydroxide is too small for accurate estimation, and consequently it is not possible to calculate its degree of dissociation and its basicity constant, nor to compare the hydroxyl-ion concentrations given by equal concentrations of ammonia and lanthana. Theoretically it is possible to compare them from a knowledge of the degrees of hydrolysis of solutions of their respective salts under absolutely identical conditions. It is extremely doubtful whether this is accomplished by Vesterberg's method on account of the different nature of the two bases, for on extracting the hydrolysed acid from a lanthanum acetate solution with ether the equilibrium is disturbed in some unknown manner. The lanthanum hydroxide, unlike the ammonium hydroxide in the case of the ammonium acetate solution, will tend to become precipitated or to pass into colloidal solution, and thereby give rise to increased hydrolysis.

The hydrogen-ion concentrations at which lanthanum and cerous hydroxides are precipitated are a little greater than that necessary for manganous hydroxide. It was therefore thought that the presence of ammonium chloride in sufficient quantity might prevent their precipitation with ammonium hydroxide (see Part I). Calculation shows that, for each molecule of ammonia, 14 and 32 molecules, respectively, of ammonium chloride should be sufficient to prevent the precipitation of lanthanum hydroxide and cerous hydroxide. Actually, ammonium chloride has some inhibiting effect on the precipitation of the two hydroxides, and when the proportion of ammonium chloride to ammonium hydroxide is large, as indicated by the calculations, the precipitation can be entirely prevented.

Summary.

Hydrogen electrode titrations of solutions of several rare-earth salts with sodium hydroxide show that:

(*a*) The order of the precipitation of the earths with alkali is samarium, yttrium, neodymium, praseodymium, tervalent cerium, and lanthanum.

(*b*) The hydrogen-ion concentrations which govern the precipitation of the hydroxides of samarium, yttrium, neodymium, and praseodymium are so very close to one another—all about 10^{-7}—that the separation of these hydroxides by fractional precipitation is not possible.

(*c*) The precipitate formed in each titration is basic.

(*d*) The precipitation p_H's of the rare earths lie below those of magnesium and manganous hydroxides and above that of zinc.

(*e*) The great difference between the hydrion concentration necessary for the precipitation of thorium hydroxide and those required in the case of the rare earths accounts for some of the processes which are used to effect its separation.

(*f*) Ammonium chloride, if present in sufficient quantity, prevents the precipitation of lanthanum and cerous hydroxides.

The author avails himself of this opportunity to thank Prof. Philip, F.R.S., for facilities in carrying out this work, the Chemical Society for a grant which covered the cost of the materials, and the Department of Scientific and Industrial Research for a personal grant.

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CCXC.—*Electrometric Studies of the Precipitation of Hydroxides. Part IV. Precipitation of Mercuric, Cadmium, Lead, Silver, Cupric, Uranic, and Ferric Hydroxides by Use of the Oxygen Electrode.*

By Hubert Thomas Stanley Britton.

Attention was directed in Part I (this vol., p. 2110) to the limited applicability of the hydrogen electrode, and consequently resort has been made to the oxygen electrode in order to study the precipitation reactions described in the following pages. Although oxygen electrodes cannot be used to follow with accuracy the changes in hydrogen-ion concentration which may take place during a reaction, they are sufficiently responsive to show the character of the changes and under certain conditions an approximate idea of the hydrogen-ion concentrations may be obtained from the titration curves. The oxygen electrode appears to have been employed for a similar purpose by Ralston (*Trans. Amer. Electrochem. Soc.*, 1923, **43**, 87), who found it of considerable use in the hydrolytic purification of electrolytes, such as the freeing of copper sulphate solutions from ferric hydroxide.

It was shown (Britton, J., 1924, **125**, 1572) in oxygen electrode titrations of chromic acid that, if the hydrogen-ion concentrations were known of solutions at two remote stages of the titration, rough estimates of the p_H of intermediate solutions could be obtained by assuming the voltages to be proportional to the p_H. This method, however, was found later to introduce errors sometimes as great as a whole p_H unit (this vol., p. 1915). The method has been further tested in the present titrations by using solutions which contained a known concentration of free acid, from which the initial p_H could be calculated, and continuing the titrations until the solutions had become alkaline and of known p_H. Table I gives particulars of the solutions titrated and the concentrations of free acid initially present. The titrations were performed with 100 c.c. of solution at 18° in each case by the method described for the previous acid titrations, the normal calomel half-element being used; as junction liquid in titrations 3 and 4 saturated potassium nitrate solution was employed instead of potassium chloride for obvious reasons. Each titration was followed by at least two oxygen electrodes and the solution was kept thoroughly mixed by a rapid current of oxygen, flowing throughout the whole titration.

The curves given by each pair of electrodes were as a rule similar, although by no means coincident, and tended to become closer to

TABLE I.

Titration and curve No.	100 C.c. of solution contained : free acid.	salt.	Sodium hydroxide. Normality.	C.c. for acid.	C.c. for salt.	Total.
1	0·0212*N*-HCl	0·02*M*-$HgCl_2$	0·1018	20·8	39·3	60·1
2	0·0199*N*-H_2SO_4	0·02*M*-$CdSO_4$	0·1018	19·6	39·3	58·9
3	0·0202*N*-HNO_3	0·02*M*-$Pb(NO_3)_2$	0·1005	20·1	39·8	59·9
4	0·0202*N*-HNO_3	0·02*M*-$AgNO_3$	0·1018	19·6	39·3	58·9
5	0·0199*N*-H_2SO_4	0·02*M*-$CuSO_4$	0·1018	19·6	39·3	58·9
6	0·0149*N*-HNO_3	0·00833*M*-$U(NO_3)_6$	0·1005	14·9	49·8	64·7
7	0·0202*N*-HCl	0·0133*M*-$FeCl_3$	0·1005	20·1	39·8	59·9

one another on repeated use; continued use, however, impaired the sensitiveness of the electrodes to changes of hydrion concentration. The differences between the typical *E.M.F.*'s given by the oxygen–normal calomel combination at the beginning and at the end of the titrations, and the corresponding *E.M.F.*'s which ordinarily would have been given by the hydrogen electrode in solutions of identical hydrion concentration, against the normal calomel half-cell, are given in Table II. These differences are, in effect, the *E.M.F.*'s of the oxygen–hydrogen cells set up in the various solutions.

TABLE II.

Titration No.	Solution.	*E.M.F.* of O_2 | solution | H_2 (volts). Beginning.	End.
1	HCl and $HgCl_2$	0·98	1·05
2	H_2SO_4 and $CdSO_4$	1·09	1·08
3	HNO_3 and $Pb(NO_3)_2$	1·04	1·05
4	HNO_3 and $AgNO_3$	0·96	1·13
5	H_2SO_4 and $CuSO_4$	0·94	1·06
6	HNO_3 and $U(NO_3)_6$	0·85	0·96
7	HCl and $FeCl_3$	0·97	1·03

Both the hydrogen-ion concentration and the oxidising agents which may be undergoing titration, have some influence on the oxygen electrode *E.M.F.* If the latter happens to be either small or almost independent of the hydrogen-ion concentration, then the proportional hydrogen-ion concentration scale may be expected to give a fairly accurate measure of the hydrion concentration. The extrapolated *E.M.F.*'s of the oxygen–hydrogen cell in the case of the uranium nitrate titration are much lower than usual, and it is probable that the small increase in potential difference was uniformly distributed over the whole titration, for the p_H's indicated by the scale at the various stages of the reaction were,

as far as could be ascertained colorimetrically, in approximate agreement. The low potential differences which were obtained in all the uranium titrations had nothing to do with the ageing of the platinum black, as in many instances freshly platinised electrodes were employed. A regular increase in the potential difference of the oxygen–hydrogen cell could not have taken place in the silver nitrate titrations, for according to the proportional hydrion scale the silver oxide was precipitated at p_H 6, whereas calculation from the solubility product of silver hydroxide showed that the true precipitation p_H lay between 9 and 10. By comparing the voltage actually observed when the precipitation began, 0·40 volt, with that which would be given by a hydrogen electrode indicating p_H 9, each compared with the normal calomel electrode, the *E.M.F.* of the oxygen–hydrogen cell is found to be 1·21 volts. This value is greater than either the initial (0·96) or the final (1·13) value, and was probably caused by the instability of the silver oxide. The remaining solutions investigated showed much less variation in their extrapolated *P.D.*'s, and when isolated p_H's were found by means of indicators and compared with those given by the scales, they were generally found to agree within half a p_H unit.

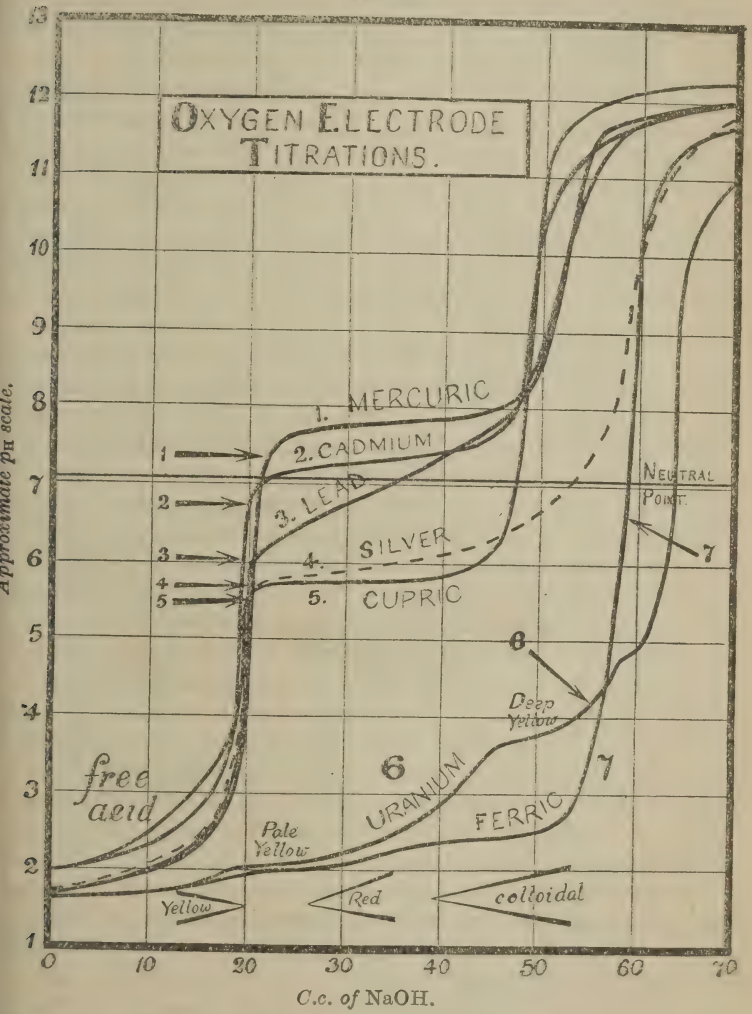
The differences in the actual voltage readings, which covered equal ranges of hydrion concentration, were usually unequal in any two titrations. Thus the change in p_H from 1·7 to 12·0 (say) would be indicated by the hydrogen and normal calomel electrodes by a variation in *E.M.F.* from — 0·381 to — 0·975 volt, a difference of 0·594 volt. In the case of the lead titration, the oxygen electrode *E.M.F.*'s moved over the same range with an almost equal change in voltage, *viz.*, from 0·667 to 0·067, a difference of 0·600 volt. In the other extreme titration, that of silver nitrate, the *E.M.F.* varied from 0·578 to 0·167 volt, a difference of 0·411 volt only.

In order to represent these titrations graphically (Fig. 1), it has been found necessary to convert the observed voltages into the approximate p_H values by simple proportion (this vol., p. 1915); these values are plotted as ordinates, and the number of c.c. of alkali added as abscissæ. Curve No. 4, representing the titration of silver nitrate, is dotted, for, as previously shown, the proportional hydrion scale is inapplicable. The arrows denote the beginning of precipitation.

The precipitation of basic mercuric chloride (curve No. 1) began when p_H 7·4 was attained; the precipitate, at first white, became brown as more alkali was added. Precipitation was complete when three-quarters of the amount of alkali required for the complete decomposition of the mercuric chloride had been added. At this point—50·3 c.c. of sodium hydroxide—the addition of more alkali

caused a rapid increase in p_H. The basic chloride was readily decomposed on the addition of an excess of alkali. The fact that exactly 1·5 equivalents of sodium hydroxide were sufficient to

FIG. 1.



transform 1 molecule of mercuric chloride completely into an insoluble basic precipitate seems to furnish good evidence that the precipitate first formed was a definite salt, *viz.*, $HgCl_2,3HgO$. Some decomposition took place immediately an excess of alkali was added, for after precipitation was complete about 2 c.c. of

alkali had to be added before the solution attained a marked alkalinity. The partial investigation by Toda (*Memoirs Coll. Sci. Kyoto*, 1921, **4**, 305) of the ternary system HgO–HCl–H_2O at 35° failed to establish the individuality of $HgCl_2,3HgO$. A crystalline basic chloride of this composition is stated to occur naturally as kleinite and mosesite, and has also been prepared by several workers (compare Mellor's " Treatise," 1923, Vol. IV, p. 842).

Curve No. 2 shows that the precipitate obtained from the cadmium sulphate solution was also basic. It was heavy and flocculent and its composition must have been $CdSO_4,3Cd(OH)_2,xH_2O$, for 49 c.c. (= 1·5 equivalents) of sodium hydroxide were required for its precipitation. Harned (*J. Amer. Chem. Soc.*, 1917, **39**, 252) arrived at the same conclusion by conductimetric titration, and Pickering (J., 1907, **91**, 1981) found that a solution of cadmium sulphate was rendered alkaline to phenolphthalein by the addition of 1·46 equivalents of alkali.

Curve No. 3, illustrating the precipitation of lead as a basic nitrate, is remarkable for the considerable change in hydrion concentration which is shown to have taken place. The mode by which the precipitate was formed is yet another example showing that precipitation is often brought about by the coagulation of a colloidal solution, initially formed. A faint opalescence occurred on the addition of 20·5 c.c. of sodium hydroxide ($p_H = 6$), but immediately after another 0·5 c.c. had been added a heavy, white precipitate appeared, only to pass, in the course of a few seconds, into colloidal solution. Further additions of alkali merely intensified the turbidity of the solution, which became opaque after the addition of 33·5 c.c. The colloidal solution coagulated when 38 c.c. of alkali had been added. Once again, 1·5 equivalents of alkali were required for complete precipitation, showing that the composition of the precipitate was $Pb(NO_3)_2,3Pb(OH)_2,xH_2O$. The existence of such a salt has been claimed by several workers.

Silver does not appear to give a basic precipitate under these conditions, as will be seen from curve No. 4.

The precipitation of basic copper sulphate is an excellent example to show how the composition of the precipitate may be influenced by the manner in which the precipitant is added. When the sodium hydroxide was added slowly to a copper sulphate solution, and the solution was thoroughly agitated, the precipitate was pale blue, amorphous, and heavy, but when the alkali was added quickly, no care being taken to ensure thorough mixing, the precipitate was green and gelatinous and, in contrast to the former precipitate, turned black either on standing or on heating. Provided the amount of alkali added was insufficient to render the solution

alkaline, the gelatinous precipitate, on shaking, gradually became converted into the less basic, amorphous precipitate. The precipitate obtained in the titration was amorphous and, as will be concluded from the amount of alkali (1·47 equivalents) required for its precipitation and to render the solution alkaline, contained CuO and SO_3 in the molar ratio 4 : 1. In his experiments on copper sulphate solutions, Pickering (*loc. cit.*) found that whilst 1·53 equivalents of sodium hydroxide actually produced complete precipitation as basic sulphate, the solution on treatment with alkali did not become alkaline to phenolphthalein until about 1·7 equivalents had been added. This initial alkalinity gradually disappeared until approximately 1·8 equivalents had been added. It is evident that Pickering obtained complete precipitation as $CuSO_4,3Cu(OH)_2,xH_2O$ in one case. The fact that the initial alkalinity did not coincide with the end of precipitation was due to the way in which the alkali was added during the testing with phenolphthalein. In the present electrometric titration, complete precipitation and alkalinity to phenolphthalein took place simultaneously. Pickering believed that the greater amount of alkali pointed to the precipitation of a mixture of basic sulphates, $4CuO,SO_3$ and $10CuO,SO_3$; the individuality of the latter he thought to be sufficiently established by the amount of alkali required to cause final alkalinity. Harned (*loc. cit.*), by titrating with a copper electrode, also found that precipitation was complete when 1·7 equivalents of sodium hydroxide had been added. Harned's observation, as was Pickering's, was due to the manner in which the precipitant was added. In a subsequent paper, it will be shown that the pale blue, amorphous precipitate is a definite basic salt, $4CuO,SO_3,4H_2O$.

The uranic solution used in the titration was prepared by dissolving so-called uranyl nitrate in nitric acid. The colour of the solution was pale yellow, but important changes in the intensity occurred during the titration. Curve No. 6 shows that a slight inflexion occurred immediately after the acid in excess of that required to form uranic nitrate had been neutralised with 14·9 c.c. of alkali; this, perhaps, may be due to the presence of sexavalent uranium nitrate in the solution (compare the titrations of the chlorides of zirconium and ferric iron). This small inflexion was repeatedly obtained. No appreciable change in colour was observed until 45 c.c. of sodium hydroxide had been added, the composition of the solute then being $U(NO_3)_{2\cdot38}(OH)_{3\cdot62}$. Thereafter the solution, though remaining clear, gradually became deeper in colour until 55·8 c.c. of alkali had reacted, the solution then containing $U(NO_3)_{1\cdot08}(OH)_{4\cdot92}$; at this stage a yellow precipitate began to

separate. It happened that this change corresponded exactly to a new section of the curve, and the point of inflexion corresponded to the solution in which the change in shade of yellow was first noticed. The diminished hydrion concentrations of the deeply coloured solutions, about p_H 3·7, were close to that at which precipitation began, p_H 4·2. The deepening in colour of the highly basic solutions seems to have been due to a gradual increase in the size of the basic particles, the uranium hydroxide being held in solution in a state closely akin to that of a colloid. The hydrion concentration of the solution when 48 c.c. of alkali had been added was $10^{-3·7}$; the solution then contained the proportions of uranium and nitrate present in uranyl nitrate but was much deeper in colour than that obtained by dissolving uranyl nitrate crystals. The explanation of this difference probably lies in the fact that uranyl nitrate is crystallised from strongly acid solutions. On solution in water, it tends to revert to a state which is probably colloidal, as shown by the changes in colour and in conductivity which it undergoes on standing and especially at higher temperatures (Dittrich, *Z. physikal. Chem.*, 1899, **29**, 449). If the increase in conductivity which takes place on standing is due to the formation of particles which are essentially colloidal, these particles must be capable of some kind of ionisation. There seems to be very little support for the belief that uranyl salt solutions contain the " uranyl " kation; none is to be found in conductivity measurements, which show that the increases in conductivity with dilution of solutions of the nitrate, chloride, and sulphate are anomalous.

The diagram shows that precipitation was complete when 64 c.c. of alkali had been added as compared with the 64·7 c.c. which were required for the complete formation of uranic hydroxide. Hence the precipitate was uranic hydroxide containing a very small quantity of undecomposed nitrate. The text-books state that alkalis precipitate " diuranates " and not uranium hydroxide; *e.g.*, with sodium hydroxide, the precipitate is stated to be $Na_2U_2O_7$ (compare Roscoe and Schorlemmer's " Treatise," Vol. II, p. 1154, revised 1923). Jolibois and Bossuet (*Compt. rend.*, 1922, **174**, 1625) found that the precipitates produced by the action of sodium hydroxide on uranyl nitrate solutions contained no nitrate; the small quantities of sodium hydroxide present, varying from 1·2 to 8% they considered to be adsorbed.

Dilute acid solutions of uranium nitrate or uranyl salt solutions themselves, when gently heated, underwent some profound change; the colour became deeper and the reverse change on cooling took place very slowly. They became alkaline to phenolphthalein when

the theoretical amount of alkali was added, but a precipitate separated only when an appreciable excess of alkali had been added or the solution had been boiled for some time. The opalescence of the alkaline colloidal solution depended on the temperature to which the original solution had been heated. The deep yellow solutions formed by gentle heating were almost clear, whereas those which had been boiled became visibly colloidal. If not too great an excess of alkali had been added, the resulting colloidal solutions remained quite stable for several days. They were coagulable on addition of 1 or 2 c.c. of saturated potassium chloride solution. Heating thus appeared to have caused some change in the state of aggregation of the particles of uranium hydroxide or more likely of highly basic salt, which were probably in equilibrium with free nitrate ions and were thereby enabled to enter into reaction with alkalis so that the uranium hydroxide complexes remained in colloidal solution.

Curve 7 represents the titration of an acid solution of ferric chloride and correlates the changes in hydrion concentration with the changes in colour. It is something more than a coincidence that the colours of solutions containing basic salts should be similar to those of their respective hydroxides. The colour of solutions of both the basic salts of chromium with strong acids and chromium hydroxide is green, and the uranium solutions are pale yellow but become intensely yellow as they become more basic and are then identical in colour with uranium hydroxide. As is well known, ferric chloride solutions freshly prepared or containing an excess of free acid, are only slightly coloured; on standing, the solution reddens and its colour approaches that of red ferric hydroxide. In the present titration the end of the neutralisation of the free acid appears to be indicated by an inflexion, at 20·1 c.c. of sodium hydroxide. As the solution was rendered more basic, the colour gradually changed from yellow to red. It became quite red after addition of 30 c.c. of sodium hydroxide, when the composition of the solute had become $Fe(OH)_{0\cdot74}Cl_{2\cdot26}$, and with 39 c.c. it began to opalesce. Afterwards the solution became increasingly colloidal and became opaque at p_H 3, which, as will be seen from the curve, occurred just when the sudden change in hydrion concentration had begun. Coagulation set in when the p_H had become 6·6 and 58 c.c. of alkali had been added, the composition of the basic chloride then being $Fe(OH)_{2\cdot85}Cl_{0\cdot15}$.

As the colloidal solution persisted until nearly all the chloride had reacted, experiments were made to see if it were possible to prevent coagulation while the solution was being subjected to a sudden fall in hydrion concentration. As in the case of basic

uranium nitrate solutions, this possibility depended on the changes which had taken place in the ferric chloride solutions before treatment with alkali. Aqueous solutions of ferric chloride more dilute than $N/25$, on boiling, acquired a deep red colour, and often remained colloidal on treatment with $N/10$-alkali in slight excess. Small, red, amorphous precipitates separated in some cases, but even then the precipitation was incomplete and the solids did not settle until several hours had elapsed. The presence of a little hydrochloric acid in the solutions before heating had some stabilising effect on the colloidal solutions which were subsequently produced. In one case the colloidal solution remained stable for nearly 3 months. This solution was prepared by adding 55 c.c. of $N/10$-sodium hydroxide to 500 c.c. of a boiling solution containing 100 c.c. of $N/25$-ferric chloride and 10 c.c. of $N/10$-hydrochloric acid. It seems certain that the red colour of boiled ferric chloride solutions was due to dispersed ferric hydroxide particles, and consequently the increase in the size of the basic chloride particles caused by rendering the solution alkaline was not so great as that occurring in an unboiled solution, and therefore did not produce coagulation. The increased stability of the colloidal solutions prepared from acidified ferric chloride solutions was probably due to the effect of the acid in suppressing the growth of the colloidal particles on boiling, thereby giving rise to a more highly dispersed and more stable colloidal solution. Prolonged boiling decomposed these alkaline colloidal solutions, and they were readily coagulated on addition of electrolytes in sufficient amounts.

It is probable that the solubility product of very weak bases such as ferric hydroxide has very little meaning, but in view of the recent work of Jellinek and Gordon (*Z. physikal. Chem.*, 1924, **112**, 235) it is interesting to compare their value for $[Fe^{\cdots}][OH']^3$, *viz.*, $10^{-37\cdot9}$, with that given by the titration curve. They measured the hydrogen-ion concentrations with the hydrogen electrode of solutions of ferric chloride, containing potassium chloride to coagulate the colloidal solutions, to which varying amounts of sodium hydroxide had been added. The concentration of ferric ions in the mother-liquor was determined colorimetrically as thiocyanate. The latter method is probably unsatisfactory, because the acid used would materially affect the concentration of ferric ions in a basic ferric chloride solution. If it be assumed that in the titration the appearance of opalescence marked the point at which ferric hydroxide actually began to separate, and that the amount of free ferric ions was equivalent to the remaining amount of alkali to be added to decompose the ferric chloride completely, the value for the solubility product becomes $10^{-37\cdot7}$. Thus opalescence occurred

on the addition of 39 c.c. of $N/10$-alkali; $p_H = 2{\cdot}3$. Hence $[OH'] = 10^{-11{\cdot}8}$ and $[Fe'''] = 20{\cdot}9/39{\cdot}8 \,.\, 100/139 \,.\, 0{\cdot}0133 = 10^{-2{\cdot}3}$. Müller ("Das Eisen und seine Verbindungen," 1917, p. 281) calculated the value $6{\cdot}5 \times 10^{-47}$ from Bodländer's formula (*Z. physikal. Chem.*, 1898, **27**, 66).

Arrangement of Metals in the Order of the Hydrogen-ion Concentrations required for the Precipitation of their Hydroxides.

It was stated in Part I that no principle has yet been found which leads to a satisfactory arrangement of the metals such that the order is that of the basic strengths of their hydroxides. The titrations described in the foregoing pages show that for each hydroxide there is a definite hydrogen-ion concentration at which its precipitation normally takes place. It is true that the majority of the hydroxides are thrown out of solution as basic precipitates, but the hydrogen-ion concentrations at which these are precipitated probably do not differ greatly from those of the particular hydroxides. The table gives the metals in the order of the hydrogen-ion concentrations at which their respective hydroxides are precipitated from dilute solutions. Although it is not certain that this order is that of the actual basic strengths of the hydroxides, it can be stated, as will be shown later, that it is these hydrogen-ion concentration relationships which underlie many of the reactions of the various metallic salt solutions.

Hydrion conc.		Hydrion conc.		Hydrion conc.	
10^{-11}	Magnesium		Cadmium		Copper
10^{-10}			Praseodymium		Chromium
10^{-9}	Silver		Neodymium	10^{-5}	
	Manganous		Yttrium		Aluminium
	Lanthanum	10^{-7}	Samarium	10^{-4}	
	Mercuric		Ferrous (?)		Uranic
10^{-6}	Cerous		Lead (?)		Thorium
	Cobalt	10^{-6}	Zinc	10^{-3}	
	Nickel		Beryllium		Stannous
					Zirconium
					Ferric

An arrangement now widely adopted is that based by Abegg and Bodländer (*Z. anorg. Chem.*, 1899, **20**, 453) on their theory of electroaffinity, which states that the electrolytic potential constitutes an approximate measure of the basic strength of the metal. Comparison with the present arrangement brings out the following important differences. According to the position of aluminium in the table, aluminium hydroxide is an extremely weak base, weaker than chromium hydroxide, yet aluminium occurs higher than chromium in the electropotential series. There is no doubt

that both aluminium and chromium hydroxides are much weaker bases than manganous hydroxide, and this is also indicated by the present scheme, but according to the electropotential series they are both placed above manganese. Heyrovský (*Proc. Roy. Soc.*, 1923, *A*, **102**, 628) has pointed out that the thallous potential is small, which necessitates placing thallium relatively close to hydrogen in the electropotential series, in spite of the fact that thallous hydroxide is a strong base and is not precipitated by alkalis. If it be assumed that the electrolytic potentials of metals under identical conditions are a measure of their electroaffinities, *i.e.*, the free energies by which the elements take up electric charges, it cannot be concluded, as was admitted by Abegg and Bodländer, that the potentials as determined are in any way parallel to the electroaffinities, for nothing is known of the relative atomic solubilities of the various metals in water. Unless it is known that the number of atoms of the different metals which pass into solution is the same, no guarantee can be obtained that an arrangement accruing therefrom is in any way true. Heyrovský attempted to amend the above method by introducing such factors as the mass of the kation, and obtained an order which he stated "comes out right." Heyrovský's system indicates that lead hydroxide is a stronger base than magnesium hydroxide, and that mercuric oxide is a very weak base, weaker than zinc hydroxide. The present table suggests the contrary in both cases. It is well known that water becomes alkaline (to litmus) when shaken with mercuric oxide, but remains neutral when shaken with zinc oxide.

It is probable that the present table provides as satisfactory an arrangement as any that has been hitherto advanced, as far as the general reactions which involve the strength of the base are concerned. The position of the hydroxides in the table is the important factor in processes for separating hydroxides or basic salts, as was shown to be the case in the separation of thoria from the rare earths (see Part III). The basic acetate and basic succinate methods for the separation of manganese from iron depend on the great difference in hydrogen-ion concentration required to precipitate their respective hydroxides. Lundell and Knowles (*J. Amer. Chem. Soc.*, 1923, **45**, 676) have shown that the separation may equally well be performed by fractional precipitation with ammonia in presence of ammonium chloride, the precipitation of the ferric hydroxide being controlled by rendering the solution just alkaline to methyl-red, *i.e.*, about p_H 6·3. The reason for this is apparent from the hydrion table of the hydroxides. The table also explains why mercuric oxide can be used as a separating agent for various bases. Thus E. F. Smith and Heyl (*Z.*

anorg. Chem., 1894, **7**, 87) showed that mercuric oxide caused the complete precipitation in the cold of ferric, aluminium, and chromium hydroxides, the partial precipitation of zinc, cobalt, nickel, uranium, beryllium, cerous, and lanthanum hydroxides, and failed to precipitate manganous hydroxide. The table shows that the hydrogen-ion concentration peculiar to mercuric oxide is greater than that required to precipitate manganous hydroxide, is approximately equal to that required for lanthana, is somewhat less than that required by those hydroxides which were partly precipitated, and is considerably less than that of the three bases which were completely precipitated.

Summary.

(1) The reactions between sodium hydroxide and salt solutions of certain metals have been followed with the oxygen electrode, the hydrogen electrode being inapplicable.

(2) A scale of hydrogen-ion concentrations has been applied to the observed voltages, accurate to the extent of about 0·5 p_H unit except in the case of the silver nitrate titration.

(3) Basic precipitates, probably containing definite basic salts, were obtained from solutions of mercuric chloride, copper sulphate, cadmium sulphate, and lead nitrate.

(4) The precipitate obtained from uranium nitrate solution was the hydroxide containing a little nitrate, and not sodium diuranate as is often stated.

(5) Significant changes in colour were observed in the titrations of both uranic and ferric salts.

(6) The twenty-five hydroxides which have been investigated have been arranged in the order of their respective precipitation hydrogen-ion concentrations.

In conclusion, the author wishes to thank Prof. J. C. Philip, F.R.S., for kindly placing facilities at his disposal, and the Department of Scientific and Industrial Research for a personal grant.

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CCXCI.—*The Interaction of Ethyl Acetoacetate and o-Hydroxydistyryl Ketones. Part II.*

By ISIDOR MORRIS HEILBRON, THOMAS ALFRED FORSTER, and ABRAHAM BRUCE WHITWORTH.

THE condensation of ethyl acetoacetate with *o*-hydroxydistyryl ketones was shown by Heilbron and Forster (J., 1924, **125**, 2064) to lead to the formation of *cyclo*hexenones and not, as in the case

of the *o*-hydroxymonostyryl derivatives, to pyrones. Further, it was found that the position taken up by the β-ketonic ester in the conjugated system can be arrived at owing to the fact that when it attaches itself to the styryl residue containing the *o*-hydroxyl the resulting *cyclo*hexenone is free of the carbethoxy-group. Thus, the interaction of 2′-methoxy-2-hydroxydistyryl ketone with ethyl acetoacetate leads to the formation of two *cyclo*hexenones the structures of which have been proved to be in accord with the following formulæ :

$$\begin{array}{l} \quad\quad\quad\

giving in the first place the saturated *cyclo*hexane derivative (VI), from which water can easily be removed with formation of (VII).

$$\underset{\text{(VI.)}}{\mathrm{CO_2Et{\cdot}CH{-}CO{-}CH_2 \\ Me_2N{\cdot}C_6H_4{\cdot}CH{\cdot}CH_2{\cdot}C(OH)Me}} \xrightarrow{-H_2O} \underset{\text{(VII.)}}{\mathrm{CO_2Et{\cdot}CH{-}CO{-}CH \\ Me_2N{\cdot}C_6H_4{\cdot}CH{\cdot}CH_2{\cdot}CMe}}$$

It is thus apparent that the *p*-dimethylamino-group, although normally acting as a retarding factor, does not necessarily rule out the structure given in (IV). That this truly represents the constitution of the ketone under consideration was finally proved by oxidising the *cyclo*hexenone with potassium permanganate in acetone solution, when salicylic acid was isolated from the decomposition products. That the anomalous behaviour is closely connected with the peculiar activity of the ketone is evident, for, as shown below, it disappears on methylation of the free hydroxyl group, which reaction destroys the activity of the compound (Heilbron and Buck, *loc. cit.*). Further, with 4′-dimethylamino-4-methoxy-2-hydroxydistyryl ketone, in which the "active" properties of the parent ketone are also entirely suppressed (compare Heilbron and Whitworth, J., 1923, **123**, 238), ethyl acetoacetate yields a *cyclo*hexenone with the carbethoxyl eliminated and which consequently must possess the structure (VIII).

$$\mathrm{MeO{\cdot}(HO)C_6H_3{\cdot}CH{\cdot}CH_2{\cdot}C(CH{\cdot}CH{\cdot}C_6H_4{\cdot}NMe_2){=}CH} \quad \text{(VIII.)}$$

On the other hand, the isomeric 4′-dimethylamino-3-methoxy-2-hydroxydistyryl ketone and also the 5-methoxy-compound, both of which are "active" (Heilbron and Whitworth, *loc. cit.*), yield as main products of the condensation *cyclo*hexenones similarly constituted to that obtained from 4′-dimethylamino-2-hydroxydistyryl ketone itself.

$$\mathrm{MeO{\cdot}C_6H_4{\cdot}CH{\cdot}CH_2{\cdot}C(CH{\cdot}CH{\cdot}C_6H_4{\cdot}NMe_2){=}CH} \quad \text{(IX.)}$$

$$\mathrm{Me_2N{-}\text{----------}{-}OMe} \quad \text{(X.)}$$

$$\mathrm{HO{\cdot}C_6H_4{\cdot}CH{\cdot}CH_2{\cdot}CO{\cdot}CH{\cdot}CH{\cdot}C_6H_4{\cdot}NMe_2} \quad \text{(XI.)}$$

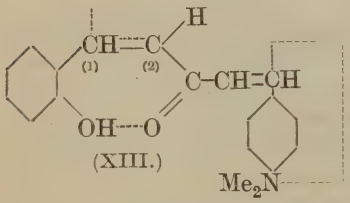
$$\mathrm{Me_2N{-}\text{----------}{-}OH} \quad \text{(XII.)}$$

With 4′-dimethylamino-2-methoxydistyryl ketone, two isomeric compounds of empirical formula $C_{26}H_{29}O_4N$ were isolated. The higher-melting *cyclo*hexenone (m. p. 164°), which is only formed in minute amount, was shown to be identical with the methyl ether of (IV) and consequently must possess the structure (X). The isomeride

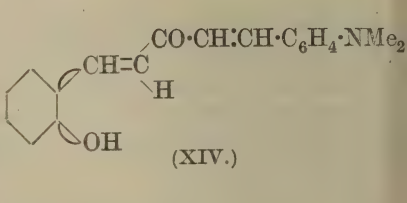
of m. p. 114° must accordingly have the constitution (IX), the reaction in this case having followed the normal course.

The primary object of the investigation has been achieved in definitely proving that, in all the cases examined, *cyclo*hexenones alone are formed as products of the condensation, and the facts harmonise well with the mechanism previously suggested to account for the elimination of carbethoxyl during the condensation (Heilbron and Forster, *loc. cit.*).

As regards the point at which ethyl acetoacetate enters the molecule, this must certainly depend largely on the polar character of the substituent groups and their total effect upon the doubly-conjugated system. The authors feel, however, that the question is too complex to allow of an immediate explanation and that no good purpose would be served by attempting this until the effect of polar influences in less complicated molecules is more thoroughly understood. It is also possible that other factors have to be taken into account and that steric influences play a part in determining the position taken up by the entering group. Thus in the case of 4′-dimethylamino-2-hydroxydistyryl ketone it is conceivable that ethyl acetoacetate, probably through the intermediate formation of a labile addition product, brings about a transformation of the co-ordinated *cis*-form of the ketone (XIII) into a *trans*-isomeride (XIV), a rearrangement which must necessarily modify the distribution of residual affinity effects.



(XIII.)



(XIV.)

This suggestion is supported to some extent by the observation recorded by Heilbron and Buck (*loc. cit.*) that, whereas 4′-dimethylamino-2-hydroxydistyryl ketone is characterised by the ease with which it forms molecular addition compounds and is indeed exceedingly difficult to isolate free from solvate addenda, this may be readily accomplished by crystallisation from ethyl acetoacetate. Again the profound effect which this ester exerts on the configuration of unsaturated ketones is exemplified in the yellow form of *o*-hydroxystyryl methyl ketone, which is readily transformed into its colourless isomeride by crystallisation from this substance (McGookin and Heilbron, J., 1924, **125**, 2099). On the other hand, ethyl cyanoacetate does not induce isomerism of this type (unpublished work)

and it might consequently be expected that in this case addition would take place at the usually reactive unsaturated centre. In presence of 50% sodium hydroxide a condensation product of empirical formula $C_{22}H_{23}O_6N$ was isolated to which either formula (XI) or (XII) could be ascribed. That the former correctly represents the structure of the compound was shown by treatment of the dicarboxylic acid with concentrated potassium hydroxide solution, when fission of the molecule occurred with production of *p*-dimethylaminobenzaldehyde. In considering the formation of this aldehyde, it has to be borne in mind that the effect of the strong alkali might possibly produce a type of reversed Michael reaction, in which case the presence of the *p*-dimethylaminobenzaldehyde would simply result through disintegration of the distyryl ketone, fission occurring at the double bonds. That this, however, was not the case was evident from the fact that no trace of salicylaldehyde was found in the reaction mixture.

Experimental.

Ethyl 3-p-*Dimethylaminophenyl*-5-o-*hydroxystyryl*-Δ^5-cyclo*hexene*-1-*one*-2-*carboxylate* (IV).—A solution containing 4′-dimethylamino-2-hydroxydistyryl ketone (4 g.), ethyl acetoacetate (8 c.c.), absolute alcohol (20 c.c.), and potassium hydroxide solution (3 c.c. of 20%) was allowed to stand at room temperature for 24 hours. The precipitated product (2 g.) was collected and crystallised from either absolute alcohol or benzene. It separates in orange-yellow prisms (m. p. 196°) containing 1 mol. of solvent, from which it can be freed by heating in the steam-oven. It dissolves in concentrated sulphuric acid, giving the deep red solution characteristic of this type of *cyclo*hexenone (Found in material crystallised from alcohol: C, 72·0; H, 7·4; N, 3·1. $C_{25}H_{27}O_4N,C_2H_6O$ requires C, 71·9; H, 7·3; N, 3·1%. Found in material crystallised from benzene: C, 76·8; H, 6·9; N, 2·9. $C_{25}H_{27}O_4N,C_6H_6$ requires C, 77·0; H, 6·9; N, 2·9%. Found in anhydrous compound: C, 73·9; H, 6·7; N, 3·1. $C_{25}H_{27}O_4N$ requires C, 74·1; H, 6·7; N, 3·4%).

Oxidation.—About 1 g. of the substance dissolved in acetone was treated at room temperature with finely-powdered potassium permanganate, added in very small portions at a time. When the oxidation was complete, the mixture was filtered and the residue suspended in water and treated with sulphur dioxide until the manganese dioxide had dissolved. As no solid separated, the solution was made strongly acid with hydrochloric acid and ether-extracted. On removal of solvent, colourless needles were obtained and identified as salicylic acid by mixed m. p. with an authentic specimen of the acid and also by the characteristic ferric chloride coloration.

3-p-*Dimethylaminophenyl*-5-ô-*hydroxystyryl*-Δ^5-cyclo*hexene*-1-*one*-2-*carboxylic Acid*.—The previous ester was saponified by heating for 3 hours on the steam-bath with sodium hydroxide solution. The red, pasty mass was dissolved in water, and the acid precipitated by addition of dilute acetic acid. The pure compound crystallised from alcohol in yellow plates, m. p. 225° (Found : C, 73·3; H, 6·0. $C_{23}H_{23}O_4N$ requires C, 73·3; H, 6·1%).

3-p-*Dimethylamino*-5-o-*hydroxystyryl*-Δ^5-cyclo*hexene*-1-*one*.—The free acid was dissolved in glacial acetic acid and boiled for 1 hour with 20% sulphuric acid. After cooling, the green liquid was carefully neutralised with dilute alkali, and the precipitated *cyclo*hexenone crystallised from methyl alcohol, from which it separated in yellow, felted needles, m. p. 232° (Found : C, 78·9; H, 6·9. $C_{22}H_{23}O_2N$ requires C, 79·3; H, 6·9%).

Ethyl 3-p-*Dimethylamino*-5-o-*methoxystyryl*-Δ^5-cyclo*hexene*-1-*one*-2-*carboxylate* (X).—By direct methylation of the corresponding hydroxy-compound by the usual methods, only uncrystallisable products were obtained. The pure methyl ether was readily produced, however, by methylation in acetone solution according to Heilbron and Buck's method (*loc. cit.*). It separates from high-boiling ligroin in lemon-yellow prisms, m. p. 164°, and dissolves in alcoholic potash to a yellow, and in concentrated sulphuric acid to a red solution (Found : C, 74·4; H, 7·0. $C_{26}H_{29}O_4N$ requires C, 74·5; H, 6·9%).

Ethyl 3-o-*Methoxyphenyl*-5-p-*dimethylaminostyryl*-Δ^5-cyclo*hexene*-1-*one*-2-*carboxylate* (IX).—A solution of 4′-dimethylamino-2-methoxydistyryl ketone (3 g.) and 3 c.c. of ethyl acetoacetate in 10 c.c. of alcohol was heated for 3 hours on the steam-bath with potassium hydroxide solution (3 c.c. of 20%), the colour changing from deep red to orange. On gradual dilution with water a semi-solid mass was deposited which proved exceedingly difficult to crystallise, but this was finally accomplished by means of alcohol in presence of animal charcoal. Microscopic examination of the crystals revealed the presence of two substances, which were separated by repeated fractionation from carbon disulphide into a main fraction of the above ester (m. p. 112°) and a small quantity of a substance, m. p. 160°, which was identical with the methyl ether obtained by methylation of the hydroxy-*cyclo*hexenone (IV).

Ethyl 3-o-*methoxyphenyl*-5-p-*dimethylaminostyryl*-Δ^5-cyclo*hexene*-1-*one*-2-*carboxylate* can be conveniently prepared in good yield free from the higher-melting isomeride by treating an alcoholic solution of the ketone (6 g.) and ethyl acetoacetate (8 c.c.) at room temperature with potassium hydroxide solution (6 c.c. of 20%). After a few hours the red solution was inoculated with a crystal of the lower-

melting ether and kept for 2 days. The crude product (5 g.) crystallises from ether in orange needles (m. p. 114°) which are extremely hygroscopic and change colour to brick-red on standing in moist air (Found: C, 74·2; H, 7·2. $C_{26}H_{29}O_4N$ requires C, 74·5; H, 6·9%).

Ethyl 1-*Methoxy*-3-o-*methoxyphenyl*-5-p-*dimethylaminostyryl*-$\Delta^{1:5}$-cyclo*hexadiene*-2-*carboxylate*.—This substance was prepared by dissolving the corresponding *cyclo*hexenone (m. p. 114°) in sodium ethoxide solution and heating under reflux with methyl iodide for 2 hours. It separates from ether in pale yellow needles, m. p. 148° (Found: C, 74·2; H, 7·4. $C_{27}H_{31}O_4N$ requires C, 74·8; H, 7·2%).

Ethyl 3-p-*Dimethylaminophenyl*-5-p-*dimethylaminostyryl*-Δ^5-cyclo*hexene*-1-*one*-2-*carboxylate* (V).—A solution containing 3·2 g. of 4 : 4′-tetramethyldiaminodistyryl ketone (Sachs and Lewin, *Ber.*, 1902, **35**, 2576), ethyl acetoacetate (5 c.c.), and alcohol (10 c.c.) was heated under reflux for 1 hour with sodium hydroxide solution (1 c.c. of 50%). The clear red liquid was filtered from deposited sodium carbonate, and the *cyclo*hexenone, which separated on cooling, repeatedly crystallised from absolute alcohol. It forms orange-yellow needles, m. p. 174—175°; the *phenylhydrazone* melts at 239° (Found: C, 74·8; H, 7·5; N, 6·7. $C_{27}H_{32}O_3N_2$ requires C, 75·0; H, 7·4; N, 6·5%).

Ethyl 3-p-*Dimethylaminophenyl*-5-*methyl*cyclo*hexane*-5-*ol*-1-*one*-2-*carboxylate* (VI).—A hot alcoholic solution of 4-dimethylaminostyryl methyl ketone (4 g.) and ethyl acetoacetate (6 c.c.) was treated with sodium hydroxide (1 c.c. of 50%), and the resulting red solution kept for 12 hours at room temperature. The *cyclo*hexane crystallises from high-boiling ligroin in colourless needles, m. p. 149° (Found: C, 67·7; H, 8·1; N, 4·4. $C_{18}H_{25}O_4N$ requires C, 67·8; H, 7·9; N, 4·3%). The *phenylhydrazone* separates from absolute alcohol in colourless crystals, m. p. 179° (Found: N, 10·3. $C_{24}H_{31}O_3N_3$ requires N, 10·3%).

Ethyl 3-p-*dimethylaminophenyl*-5-*methyl*-Δ^5-cyclo*hexene*-1-*one*-2-*carboxylate* (VII) is formed on heating an alcoholic solution of the above compound with excess of 10% sodium hydroxide solution, when an oily mass is produced which slowly solidifies. The *cyclo*hexenone crystallises from methyl alcohol after treatment with charcoal in glistening plates, m. p. 66° (Found: N, 4·8. $C_{18}H_{23}O_3N$ requires N, 4·7%).

Ethyl 3-p-*dimethylaminophenyl*-5-(3′-*methoxy*-2′-*hydroxy*)*styryl*-Δ^5-cyclo*hexene*-1-*one*-2-*carboxylate* was prepared by boiling an alcoholic solution of 4′-dimethylamino-3-methoxy-2-hydroxydistyryl ketone (5 g.) and ethyl acetoacetate (2 mols.) for 3 hours under reflux with sodium hydroxide solution (3 c.c. of 40%). After removal of inor-

ganic material by filtration, the crude *cyclo*hexenone was purified by repeated crystallisation first from absolute alcohol and finally from high-boiling ligroin. It forms yellow crystals, m. p. 197—198°, readily soluble in chloroform and benzene, sparingly soluble in alcohol (Found : C, 71·6; H, 6·5. $C_{26}H_{29}O_5N$ requires C, 71·8; H, 6·7%).

3-(4′-*Methoxy*-2′-*hydroxy*)*phenyl*-5-p-*dimethylaminostyryl*-Δ^5-cyclo*hexene*-1-*one*.—An alcoholic solution containing 4′-dimethylamino-4-methoxy-2-hydroxydistyryl ketone (6 g.) and ethyl acetoacetate (8 g.) was heated for ½ hour on the steam-bath with 6 c.c. of 50% sodium hydroxide. After cooling, the solution was filtered from a small quantity of material which could not be further purified, and the filtrate diluted with water. The red, amorphous solid thus obtained was dried and repeatedly crystallised from benzene. The pure *cyclo*hexenone forms orange-red crystals, m. p. 218° (Found : C, 75·8; H, 6·9. $C_{23}H_{25}O_3N$ requires C, 76·0; H, 6·9%).

Ethyl 3-p-*Dimethylaminophenyl*-5-(5′-*methoxy*-2′-*hydroxy*)*styryl*-Δ^5-cyclo*hexene*-1-*one*-2-*carboxylate*.—4′-Dimethylamino-5-methoxy-2-hydroxydistyryl ketone (4 g.) and ethyl acetoacetate (8 g.) were treated in alcoholic solution with aqueous sodium hydroxide (8 c.c. of 20%). After 3 days, the solution was filtered from a small quantity of solid, and the filtrate slowly diluted with water, when the *cyclo*hexenone ester was precipitated. It crystallises from benzene with 1 mol. of solvent of crystallisation in yellow crystals, m. p. 196—197° (Found : C, 74·9; H, 7·2. $C_{26}H_{29}O_5N,C_6H_6$ requires C, 74·8; H, 6·8%). The residue was washed with water to remove inorganic material and crystallised from aqueous pyridine. It separated in orange crystals, m. p. 250°. Analysis of this compound shows that the carbethoxyl has been split off, from which it follows that its structure corresponds to 3-(5′-methoxy-2′-hydroxy)-phenyl-5-*p*-dimethylaminostyryl-Δ^5-*cyclo*hexene-1-one (Found : C, 75·9; H, 6·9. $C_{23}H_{25}O_3N$ requires C, 76·0; H, 6·9%).

γ-p-*Dimethylaminocinnamoyl*-β-o-*hydroxyphenylpropane*-αα′-*dicarboxylic Acid* (XI).—A mixture containing 4′-dimethylamino-2-hydroxydistyryl ketone (8·2 g. of chloroform addition product) and 8 c.c. of ethyl cyanoacetate in 25 c.c. of hot alcohol was treated with sodium hydroxide solution (8 c.c. of 50%), when a deep red coloration rapidly developed and ammonia was evolved. After 16 hours the reaction mixture was filtered from tarry and inorganic material, diluted to 2000 c.c., and the clear orange-red solution rendered acid with dilute acetic acid. As an examination of the precipitated product after crystallisation from benzene indicated that two substances were present, the whole was boiled with sodium hydroxide solution until all evolution of ammonia had ceased. After again

rendering acid, the precipitated product was purified by repeated crystallisation from nitrobenzene, when glistening, orange needles, m. p. 220°, were obtained (Found: C, 66·3; H, 5·8. $C_{22}H_{23}O_6N$ requires C, 66·5; H, 5·8%). That the ethyl cyanoacetate had entered the molecule at positions 1 and 2 (XIII) was proved by slowly running a concentrated alkaline solution of the acid from a dropping-funnel on to boiling potassium hydroxide solution (50 c.c. of 70%) contained in a distillation flask, fitted with a condenser. Pale green crystals (m. p. 66°) separated from the collected steam distillate and were identified as *p*-dimethylaminobenzaldehyde by mixed m. p. determinations with an authentic specimen and by the formation of the phenylhydrazone. The residue left in the flask was carefully examined for the presence of salicylaldehyde, but no trace either of this or of salicylic acid could be found.

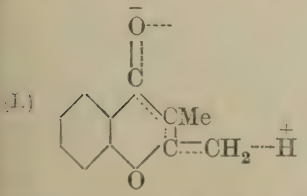
The authors desire to thank the Council of the Department of Scientific and Industrial Research for a grant in aid to one of them (T. A. F.) which has enabled this work to be carried out.

The University, Liverpool. [*Received, July 10th*, 1925.]

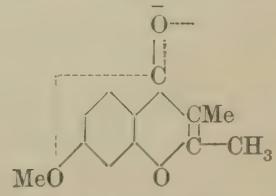
CCXCII.—*Chemical Reactivity and Conjugation. Part II. The Reactivity of the 2-Methyl Group in the 4-Quinazolone Series.*

By Isidor Morris Heilbron, Francis Noel Kitchen, Edward Burdon Parkes, and George Donald Sutton.

It has previously been demonstrated (Heilbron, Barnes, and Morton, J., 1923, **123**, 2559) that the reactivity of the 2-methyl group in 2 : 3-dimethylchromone is conditioned by its capacity to pass into the activated polarised form (I) and that this effect can be entirely suppressed by replacement of hydrogen for methoxyl in position 7, the substituted 7-methoxy-2 : 3-dimethylchromone (II) being entirely unreactive owing to neutralisation of partial valency forces.



(I.)

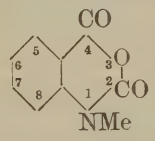


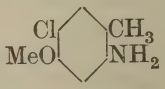
(II.)

The examination of this phenomenon has now been extended to the 4-quinazolone series, which has been widely investigated by

Bogert and his collaborators. That 2 : 3-dimethyl-4-quinazolone (V) contains a reactive methyl group has been demonstrated by the preparation of 2-styryl-3-methyl-4-quinazolone (Bogert, Beal, and Amend, *J. Amer. Chem. Soc.*, 1910, **32**, 1654) and we have now been able to show that the isomeric 1 : 2-dimethyl-4-quinazolone (VI) also is capable of yielding styryl derivatives.

This latter compound was first prepared by Weddige (*J. pr. Chem.*, 1887, **36**, 152) by direct methylation of anthranilamide followed by acetylation and subsequent loss of water from the acetyl methyl derivative. On testing this method, it was found that the yield of methylanthranilamide produced was poor owing to simultaneous formation of anthranilamide dimethyl ether. Other methods were therefore sought, starting from methylanthranilic acid itself. As distillation of the ammonium salt failed to yield the amide, an attempt was made to obtain the 1 : 2-dimethyl-4-quinazolone directly by distillation of the ammonium salt of acetylmethylanthranilic acid, but although some of the desired substance was obtained the yield was again unsatisfactory.

(III.) 



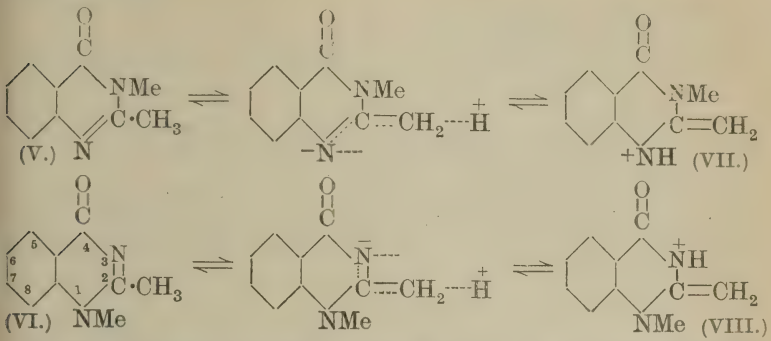
(IV.)

As these methods failed to give the required amide, attention was next directed to an investigation of Niementowski and Rozanski (*Ber.*, 1889, **22**, 1672), who found that isatoic anhydride was readily converted into anthranilamide by 0·88 ammonia. The preparation of methylisatoic anhydride (III) proved a simple matter, a quantitative yield of this substance being obtained on treatment of methylanthranilic acid successively with chloroformic ester and acetyl chloride (compare Bredt and Hof, *Ber.*, 1900, **33**, 27). With concentrated ammonia, it passes readily into methylanthranilamide, a reaction which incidentally furnishes fresh proof of the correctness of the anhydride structure of isatoic acid (compare Erdmann, *Ber.*, 1899, **32**, 2159).

As in the case of 2 : 3-dimethylchromone, both the 1 : 2-dimethyl-4-quinazolone and the isomeric 2 : 3-dimethyl compound readily condense at room temperature with aromatic aldehydes in presence of alcoholic sodium ethoxide to yield 2-styryl derivatives, the more drastic conditions of boiling the reactants together as employed by Bogert, Beal, and Amend (*loc. cit.*) being unnecessary.

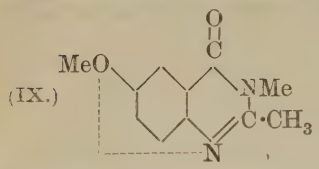
In both these compounds we consider that the reactivity of the methyl group is conditioned by the tendency of the unsaturated nitrogen atoms, as with the carbonyl oxygen atom of 2 : 3-dimethyl-

chromone, to acquire a slight negative charge, thus producing an activated phase of the molecule which, in its final state, may be represented as completed isomeric change into the methylene forms (VII and VIII).

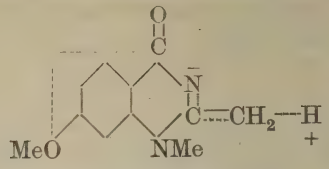


It will be observed that in the case of VI a conjugated system, analogous to that contained in 2 : 3-dimethylchromone, is present and it is thus conceivable that, if the activity is conditioned by the presence of this system, substitution of methoxyl for hydrogen in the 7-position might be capable of suppressing the reactivity of the 2-methyl group owing to neutralisation of valency forces. In order experimentally to test this point, 7-methoxy-1 : 2-dimethyl-4-quinazolone was prepared from 4-methoxyanthranilic acid (Ullmann and Dootson, *Ber.*, 1918, **51**, 9) by a series of reactions similar to those detailed in the preparation of the unsubstituted 1 : 2-dimethyl-4-quinazolone. On treatment of this compound with piperonal in presence of alcoholic sodium ethoxide a styryl derivative was readily formed, thus showing that the reactivity of the 2-methyl group in this case is dependent mainly on the activation of the nitrogen atom in position 3. 7-Methoxy-2 : 3-dimethyl-4-quinazolone has also been prepared and, as was to be anticipated, proved to be a reactive substance, the reactivity in this case being conditioned by the nitrogen atom in position 1. An examination of the formula representing the polarised form of 2 : 3-dimethyl-4-quinazolone reveals the fact that in the case of 6-methoxy-2 : 3-dimethyl-4-quinazolone there is a possibility of complete neutralisation of valency forces being effected (IX), and if this occurred the nitrogen atom in position 1 would be rendered inactive. The preparation of this compound and also the isomeric 6-methoxy-1 : 2-dimethyl-4-quinazolone was carried out as described in the experimental portion. Under no conditions, however, could 6-methoxy-2 : 3-dimethyl-4-quinazolone be induced to condense with aromatic aldehydes, the compound being recovered unchanged even when the reactants were heated to high temperatures in presence of a con-

densing agent. On the other hand, 6-methoxy-1 : 2-dimethyl-4-quinazolone, which is incapable of forming a closed valency



(IX.)



(X.)

circuit, readily yields styryl derivatives when an alcoholic solution of the components is treated with sodium ethoxide.

As regards the degree of activity noted, it appears general that the 1 : 2-dimethyl-4-quinazolones are more reactive than the corresponding 2 : 3-dimethyl isomerides. This enhanced effect is probably due to the presence of the conjugated system $O{=}C{-}N{=}C{\cdot}CH_3$ in the former series, and in agreement with this it is found that a certain retardation of activity is noticeable in the case of 7-methoxy-1 : 2-dimethyl-4-quinazolone, thus showing that neutralisation effects (X), although not sufficient to prevent reaction, do nevertheless come into play.

An interesting point worthy of record was noted during the preparation of 4-methoxyanthranilic acid from *o*-nitro-*p*-cresol methyl ether. Ullmann and Dootson recommend direct oxidation of this compound to the corresponding 2-nitro-4-methoxybenzoic acid with subsequent reduction to the anthranilic acid. As this method is somewhat laborious, attempts were made first to reduce the nitrocresol methyl ether to the amino-compound and then to oxidise the acetylamino-derivative to the acid as detailed by Friedländer, Buchner, and Deutsch (*Annalen*, 1912, **388**, 44). *o*-Amino-*p*-cresol methyl ether was first prepared by Knecht (*Annalen*, 1882, **215**, 83) by reduction of *o*-nitro-*p*-cresol methyl ether with tin and hydrochloric acid and described as a colourless solid, m. p. 47°. On repeating this experiment, an amine (m. p. 112°) was obtained from the steam distillate, which after recrystallisation melted at 116°, and was apparently identical with the compound, m. p. 111°, originally obtained by Limpach (*Ber.*, 1889, **22**, 791; 1891, **24**, 4136). On examination of this substance, we found that it is actually a chlorinated amine to which the constitution IV has been assigned, the reaction obviously having followed a similar course to that occurring during the reduction of *p*-nitrophenetole under similar conditions (Hurst and Thorpe, J., 1915, **107**, 924).

Experimental.

2 : 3-*Dimethyl*-4-*quinazolone* was prepared in good yield by treatment of acetanthranil with methylamine solution according to

Bogert and Seil's method (*J. Amer. Chem. Soc.*, 1907, 29, 529). It forms colourless needles (from water) containing 1 mol. of solvent, m. p. 72°. The anhydrous compound is obtained by heating in the steam-oven and melts at 112°.

Condensation Products.—In all cases, unless otherwise stated, these were prepared by allowing an alcoholic solution of the reactants to stand at room temperature in presence of sodium ethoxide as condensing agent. The styryl derivative either separates out directly from the alcoholic solution or on dilution with water.

2-*Styryl*-3-*methyl*-4-*quinazolone* was originally prepared by Bogert, Beal, and Amend (*loc. cit.*) by boiling 2 : 3-dimethyl-4-quinazolone with benzaldehyde. It is also readily produced by the method described above and forms pale yellow, silky needles, m. p. 167° (Bogert gives 170°).

4′-*Methoxy*-2-*styryl*-3-*methyl*-4-*quinazolone* forms bright yellow needles from alcohol, m. p. 146°, soluble in dilute hydrochloric acid, giving an orange-coloured solution (Found : N, 9·5. $C_{18}H_{16}O_2N_2$ requires N, 9·6%).

3′ : 4′-*Dimethoxy*-2-*styryl*-3-*methyl*-4-*quinazolone* separates in yellow plates from benzene, m. p. 208° (Found : N, 8·6. $C_{19}H_{18}O_3N_2$ requires N, 8·7%).

3′ : 4′-*Methylenedioxy*-2-*styryl*-3-*methyl*-4-*quinazolone* forms bright yellow needles, m. p. 185° (Found : N, 9·0. $C_{18}H_{14}O_3N_2$ requires N, 9·2%).

4′-*Dimethylamino*-2-*styryl*-3-*methyl*-4-*quinazolone* crystallises from alcohol in orange-red needles, m. p. 175°. The solution in dilute hydrochloric acid is dark red (Found : N, 13·8. $C_{19}H_{19}ON_3$ requires N, 13·8%).

Methylisatoic anhydride was produced from methylanthranilic acid according to the method employed by Bredt and Hof (*loc. cit.*) for the production of isatoic anhydride. The acid was refluxed with chloroformic ester (3 mols.) until a clear solution resulted, after which a slight excess of acetyl chloride was added and the heating continued until all evolution of hydrogen chloride had ceased. On cooling, *methylisatoic anhydride* separated in quantitative yield in colourless prisms, m. p. 180° (Found : N, 7·9. $C_9H_7O_3N$ requires N, 7·9%).

The *carbethoxy*-derivative of methylanthranilic acid forms colourless crystals, m. p. 108° (Found : N, 6·4. $C_{11}H_{13}O_4N$ requires N, 6·3%).

Methylanthranilamide was produced in quantitative yield by boiling methylisatoic anhydride with 0·88 ammonia. The thick, white precipitate was filtered off and crystallised from alcohol, from which the pure amide separated in colourless needles, m. p. 162°.

1 : 2-*Dimethyl*-4-*quinazolone* was obtained in excellent yield by

boiling *N*-methylanthranilamide with excess of acetic anhydride until the volume of the solution had been reduced to about one-half, after which it was diluted with water, rendered alkaline, and again boiled for about 10 minutes. The crude quinazolone separated on cooling and was purified by crystallisation from water, forming silky needles containing water of crystallisation. The anhydrous compound (m. p. 203°) is obtained by heating in the steam-oven (Weddige gives 199°).

2-*Styryl*-1-*methyl*-4-*quinazolone* crystallises from aqueous alcohol in cream-coloured needles, m. p. 245° (Found : N, 10·8. $C_{16}H_{13}ON_2$ requires N, 10·7%).

4′-*Methoxy*-2-*styryl*-1-*methyl*-4-*quinazolone* forms bright yellow needles from aqueous alcohol, m. p. 94°, containing $2H_2O$. The anhydrous compound melts at 156° and dissolves in dilute hydrochloric acid with a deep yellow colour (Found : N, 9·6%). 3′ : 4′-*Methylenedioxy*-2-*styryl*-1-*methyl*-4-*quinazolone* forms yellow needles, m. p. 264° (Found : N, 9·1%). 4′-*Dimethylamino*-2-*styryl*-1-*methyl*-4-*quinazolone* forms orange needles, m. p. 274°. The solution in dilute hydrochloric acid is bright red (Found : N, 13·7%).

6-*Nitro*-3-*hydroxybenzaldehyde*.—*m*-Hydroxybenzaldehyde was nitrated as detailed by Pschorr (*Annalen*, 1912, **391**, 28). The crude nitration product was boiled under reflux with four times its weight of benzene for ½ hour, allowed to cool to 50°, and rapidly filtered. Employing this temperature instead of the lower temperature of 45° used by Pschorr rendered the separation much more complete. 6-Nitro-3-hydroxybenzaldehyde * separates from boiling water in long, yellow needles, m. p. 166° (yield 34% of theory).

6-*Nitro*-3-*methoxybenzaldehyde* was originally obtained by Pschorr, but no details of his method are given. A 95% yield of the ether is readily obtained by the following procedure : 6-Nitro-3-hydroxybenzaldehyde (50 g.) was dissolved in the calculated amount of potassium hydroxide solution and warmed at 60°, after which methyl sulphate (56 c.c.) was added and the mixture well shaken. After cooling, the solution was made alkaline; the methyl ether, which rapidly separated, crystallised from alcohol in colourless needles, m. p. 82°.

6-*Nitro*-3-*methoxybenzoic Acid*.—The oxidation of the aldehyde was carried out by suspending it (20 g.) in 1500 c.c. of warm dilute potassium hydroxide solution (1 mol. KOH) and gradually adding the calculated amount of a 2% solution of potassium permanganate, the whole being mechanically stirred. The alkaline filtrate was

* The preparation of this compound in good yield (87%) has been much simplified by Mason (this vol., p. 1195), whose paper appeared after the completion of the work described in this communication.

rendered acid, the solution saturated with salt and ether-extracted. After removal of solvent the crude acid was crystallised from alcohol, separating in colourless needles, m. p. 97° (yield 87%). It is essential to employ the pure aldehyde in this oxidation, otherwise the yield of acid is largely reduced. This substance was found to contain 1 mol. of water of crystallisation, the anhydrous acid which is obtained by heating in the steam-oven melting at 133° as given by Pschorr.

5-*Methoxyanthranilic acid* was prepared by Pschorr (*loc. cit.*) by reduction of the nitro-acid with ferrous sulphate and ammonia. A more satisfactory method is to carry out the reduction by means of stannous chloride and concentrated hydrochloric acid, when a 75% yield of the required acid results.

5-*Methoxyacetanthranil*.—The method employed was similar to that described by Bogert (*J. Amer. Chem. Soc.*, 1911, **33**, 949). 5-Methoxyanthranilic acid was gradually added to excess of boiling acetic anhydride, when a vigorous reaction occurred with precipitation of a yellow solid which dissolved on further heating. On allowing the solution to cool, the anthranil was deposited in quantitative yield. It crystallises from benzene in colourless, prismatic needles, m. p. 124° (Found : N, 7·5. $C_{10}H_9O_3N$ requires N, 7·3%).

6-*Methoxy*-2-*methyl*-4-*quinazolone*.—On boiling the anthranil for 1 hour under reflux with a large excess of 0·88 ammonia, it gradually dissolved and as the reaction proceeded the quinazolone separated out. It forms glistening needles (from aqueous alcohol), m. p. 270° (Found : N, 14·7. $C_9H_{10}O_2N_2$ requires N, 14·7%).

6-*Methoxy*-2 : 3-*dimethyl*-4-*quinazolone* was prepared in an analogous manner by employing alcoholic methylamine solution and was also easily obtained by the action of methyl sulphate on an alkaline solution of the 2-methylquinazolone. It separates from boiling water in colourless needles containing 1 mol. H_2O, m. p. 87°. The anhydrous compound is readily formed on heating the hydrated substance in a steam-oven and melts at 133° (Found : N, 13·9. $C_{11}H_{12}O_2N_2$ requires N, 13·7%).

Attempts were made to condense this quinazolone with aromatic aldehydes by condensation in presence of alcoholic sodium ethoxide both in the cold and heat, but in each case unchanged substance was recovered. The quinazolone was also heated with piperonal alone under precisely similar conditions to those employed by Bogert (*loc. cit.*), but on extracting the melt practically the whole of it was recovered unchanged. This experiment was repeated in presence of zinc chloride as condensing agent, but here again unchanged quinazolone was obtained.

5-*Methoxymethylanthranilic acid* was prepared according to

Willstätter and Kahn's method (*Ber.*, 1904, **37**, 408) by direct methylation of the sodium salt of the acid with methyl sulphate in the cold. It separates from benzene after treatment with animal charcoal in yellow needles, m. p. 163°. Both the ethereal and the aqueous solution exhibit a strong blue fluorescence (Found : N, 7·7. $C_9H_{11}O_3N$ requires N, 7·7%).

6-*Methoxymethylisatoic anhydride* was prepared as previously described. It crystallises from acetone in colourless needles, m. p. 233° (Found : N, 6·6. $C_{10}H_9O_4N$ requires N, 6·8%). On refluxing with excess of 0·88 ammonia, it is converted into 5-*methoxymethylanthranilamide*, which separates from boiling water in colourless needles, m. p. 145° (Found : N, 15·5. $C_9H_{12}O_2N_2$ requires N, 15·6%).

6-*Methoxy*-1 : 2-*dimethyl*-4-*quinazolone*.—On treatment of the amide with acetic anhydride as described in the preparation of the unsubstituted 1 : 2-dimethyl-4-quinazolone, it is quantitatively converted into 6-methoxy-1 : 2-dimethyl-4-quinazolone, which crystallises from water in long, colourless needles, m. p. 220° (Found : N, 13·8%).

6-*Methoxy*-3′ : 4′-*methylenedioxy*-2-*styryl*-1-*methyl*-4-*quinazolone*.—Unlike the inactive isomeric 6-methoxy-2 : 3-dimethyl-4-quinazolone, the 1 : 2-dimethyl compound reacts readily with aromatic aldehydes, the condensation with piperonal being completed in the cold after 12 hours. By warming on the water-bath the reaction is much accelerated, the condensation product commencing to separate after 10 minutes. The crude product was purified by recrystallisation from alcohol and formed microscopic, yellow needles, m. p. 284° (Found : N, 8·2. $C_{19}H_{16}O_4N_2$ requires N, 8·3%).

4-*Methoxymethylanthranilic acid* was prepared from 4-methoxyanthranilic acid by direct methylation with methyl sulphate. It separates from alcohol in colourless needles, m. p. 165° (Found : N, 7·8%). The conversion of this acid into 7-*methoxymethylisatoic anhydride* follows the directions previously given. The substance crystallises from acetone in colourless prisms, m. p. 200° (Found : N, 6·9%). On treatment with 0·88 ammonia it is quantitatively converted into 4-*methoxymethylanthranilamide*, which crystallises from alcohol in colourless needles, m. p. 138° (Found : N, 15·6%).

7-*Methoxy*-1 : 2-*dimethyl*-4-*quinazolone* was prepared in an analogous manner to that of the isomeric 6-methoxy-compound, and after treatment with animal charcoal separated from absolute alcohol in colourless crystals, m. p. 193°. It crystallises from water with 1 mol. H_2O and melts indefinitely at about 135° (Found : N, 12·6. $C_{11}H_{12}O_2N_2$, H_2O requires N, 12·6%).

7-*Methoxy*-3′ : 4′-*methylenedioxy*-2-*styryl*-1-*methyl*-4-*quinazolone* forms yellow needles (from ethyl alcohol), m. p. 280° (Found : N, 8·3%)

7-*Methoxy*-4′-*dimethylamino*-2-*styryl*-1-*methyl*-4-*quinazolone* is best prepared by refluxing an alcoholic solution of the constituents in presence of sodium ethoxide and precipitating the styryl derivative with water. It separates from alcohol in bright red cubes, m. p. 266° (Found : N, 12·8. $C_{20}H_{19}O_2N_3$ requires N, 12·5%).

4-*Methoxyacetanthranil*, prepared by boiling 4-methoxyanthranilic acid with excess of acetic anhydride, crystallises from water in colourless needles, m. p. 128° (Found : N, 7·4%).

7-*Methoxy*-2-*methyl*-4-*quinazolone* prepared by the usual method crystallises from alcohol in colourless needles, m. p. 272° (Found : N, 14·6. $C_{10}H_{10}O_2N_2$ requires N, 14·7%). On treatment with methyl sulphate it is immediately converted into 7-*methoxy*-2 : 3-*dimethyl*-4-*quinazolone*. This substance is equally readily prepared by the direct treatment of 4-methoxyacetanthranil with methylamine solution, a reaction which definitely fixes its constitution. The quinazolone crystallises from water with 1 mol. H_2O in colourless needles, m. p. 80°. The anhydrous compound melts at 149° Found : N, 13·7. $C_{11}H_{12}O_2N_2$ requires N, 13·7%).

7-*Methoxy*-3′ : 4′-*methylenedioxy*-2-*styryl*-3-*methyl*-4-*quinazolone* separates from alcohol in yellow crystals, m. p. 193° (Found : N, 9·3%).

5-*Chloro*-2-*amino*-4-*methoxytoluene*.—*o*-Nitro-*p*-cresol methyl ether was reduced by warming with tin and concentrated hydrochloric acid in the usual manner, the solution diluted with water, rendered alkaline, and subjected to steam distillation. The amine (m. p. 112°) crystallised from benzene in colourless plates, m. p. 116° (Found : N, 8·5. $C_8H_{10}ONCl$ requires N, 8·2%). The *acetyl* derivative melts at 183—184° (Found : N, 6·8. $C_{10}H_{12}O_2NCl$ requires N, 6·6%).

In conclusion, we desire to thank the Directors of the United Alkali Company for a grant to one of us (F.N.K.) which has enabled this work to be carried out.

The University, Liverpool. [*Received, July 10th*, 1925.]

NOTES.

Preparation of the Phenylcarbamyl Derivatives of Nitrophenols.

By Oscar L. Brady and Jack Harris.

Nitrophenols do not react readily with phenylcarbimide and the following method for the preparation of their phenylcarbamyl derivatives is an improvement on those previously described (Dumpert, *J. pr. Chem.*, 1885, **32**, 278; Michael and Cobb, *Annalen*,

1908, **363**, 91; Vallée, *Ann. Chim. Phys.*, 1908, **15**, 331; Busche, Blume, and Pungs, *J. pr. Chem.*, 1909, **79**, 534).

The nitrophenol (4·8 g.) is gently boiled with phenylcarbimide (5 g.) in toluene under reflux for 3 hours. On cooling, the phenylcarbamyl derivative crystallises; in the case of *o*-nitrophenol it may be necessary to boil off some toluene, as its derivative is considerably more soluble than the others. After being washed with cold 2*N*-sodium hydroxide and crystallised once from chloroform the pure nitrophenyl phenylcarbamates are obtained. *m-Nitrophenyl phenylcarbamate* forms bulky, colourless needles, m. p. 129° (Found: N, 11·1. $C_{13}H_{10}O_4N_2$ requires N, 10·9%).—University College, London. [*Received, July 21st*, 1925.]

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d-*Mannitol from* Gardenia turgida. By Martin Onslow Forster and Keshaviah Aswath Narain Rao.

On requesting Mr. R. S. Pearson, C.I.E., Forest Economist, Dehra Dun, to supply Dekamali resin in quantity sufficient for completing the investigation of gardenin, it was found that this gum from *Gardenia lucida* was extremely scarce; but we were supplied instead with an exudation from *G. turgida* entirely different in appearance and properties from the material examined by Stenhouse (*Annalen*, 1856, **98**, 316; Stenhouse and Groves, *ibid.*, 1880, **200**, 311). The product from *G. turgida* has a faintly pleasant smell in place of the odour suggesting cat's urine, and consists of loose fragments in which colourless crystals can be recognised under the lens. It dissolves almost completely in cold water with slight frothing, forming a pale brown, viscous liquid, slow to filter and depositing a brown syrup on evaporation. Furfurol is not produced on boiling with hydrochloric acid, and the tests for nitrogen, aldehydes, and ketones were negative.

The powdered substance (50 g.) dissolved in water (200 c.c.) was shaken with tribasic lead acetate (15 g.) added in small quantities, and filtered after 20 hours, when the lead was precipitated completely by hydrogen sulphide; the concentrated filtrate from lead sulphide deposited silky, white needles identified as *d*-mannitol (dimorphous, soft needles or hard prisms; m. p. 165—166°, unchanged by admixture with *d*-mannitol; solubility 14·7 parts in 100 H_2O at 19°; $[\alpha]_D$ in borax solution, 19·7°; m. p. of hexa-acetyl derivative, 120°). The yield corresponds to about 40% of the dried exudation.

Our thanks are due to Mr. R. S. Pearson for kindly supplying us with this material.—Indian Institute of Science, Bangalore, S. India. [*Received, June 29th*, 1925.]

CCXCIII.—*The Velocity of Benzylation of certain Amines. Part II.*

By David Henry Peacock.

In a previous paper (J., 1924, **125**, 1975), the energies of activation for the reaction between benzyl chloride and aniline or *p*-toluidine, and between *p*-nitrobenzyl chloride and aniline or *p*-toluidine were calculated from the velocity coefficients at two temperatures; no evidence was found that these energies are additive in character. The results of some further experiments are now described, but before their bearing on the nature of the process of activation is discussed the effect of substitution and other factors will be dealt with.

m-Nitrobenzyl chloride always reacted faster than *p*-nitrobenzyl chloride with the bases used. Olivier (*Rec. trav. chim.*, 1922, **41**, 646) obtained similar results in their hydrolysis. Slator and Twiss (J., 1909, **95**, 99) found that the order was reversed with sodium thiosulphate, where reaction is taking place with the negative thiosulphate ion. These results can be explained on the alternate polarity hypothesis. With bases such as aniline and dimethylaniline nitrobenzyl chlorides react more slowly than does benzyl chloride, although it might be expected that the general polar effect of the nitro-group would make the chlorine more reactive in nitrobenzyl than in benzyl chloride. These results may be explained by assuming that before reaction occurs the base and the halogen compound combine loosely and the negative substituent in the benzyl chloride then weakens the tendency of the nitrogen to form part of a positive ion and so reduces the rate of reaction. The results of other experiments described below show that the introduction of a nitro-group into the nucleus of the base considerably reduces the reaction velocity.

Additional evidence in support of this assumption can be obtained from the results of Jones and Preston (J., 1912, **101**, 1931) and of Thomas (J., 1913, **103**, 595), who obtained the following velocity coefficients in alcohol at 40° with dimethylaniline: benzyl bromide 6·34, *m*-xylyl bromide 8·62, *p*-xylyl bromide 23·2, *p*-bromobenzyl bromide 6·03. The positively substituted benzyl bromide reacts faster, and the negatively substituted benzyl bromide more slowly, than the unsubstituted bromide.

The effect of substitution in the nucleus of the base upon the velocity coefficient can be seen from the data given later. *m*-Nitroaniline reacts faster than *p*-nitroaniline, and *p*-toluidine faster than *o*-toluidine; results in accordance with the alternate polarity hypothesis.

The effect of concentration on the velocity coefficients and energies

of activation is sometimes considerable and, as will be seen from the tabulated results, depends on the character of the base employed. Attention is also directed to the difference in the effect of alteration in concentration upon the velocity and energy of activation of the reaction between benzyl chloride and dimethylaniline.

Velocity coefficient and concentration.

Base.	Conc.	Conc. of benzyl chloride.	$k_{35°} \times 10^3$.	$k_{45°} \times 10^3$.	E, calories.
Aniline	0·4	0·2	3·62	8·5	16550
	0·8	,,	3·68	9·2	17770
	1·6	,,	4·07	10·55	18460
	1·6	0·4	4·25	11·2	18780
o-Toluidine	0·8	0·2		5·96	
	1·6	,,		7·1	
p-Toluidine	0·8	,,	5·96	14·7	17440
	1·6	,,	6·21	15·1	17230
p-Chloroaniline	0·4	,,		5·15	
	0·8	,,		5·08	
Monoethylaniline.....	0·8	,,		1·138	
	1·6	,,		1·13	
Dimethylaniline	0·8	,,	2·78	6·09	15210
	1·6	,,	2·23	5·06	15890
Diethylaniline	0·8	,,		0·400	
	1·6	,,		0·303	

Examination of the results obtained showed also an interesting connexion between energy of activation and the constitution of the substituted benzyl chloride used. When the energies of activation of *m*- and *p*-nitrobenzyl chlorides with aniline, *p*-toluidine, *o*-toluidine, and dimethylaniline are compared, it is seen that, although there is apparently no strictly quantitative additive relation, there is a qualitative relationship, the energy of activation for *m*-nitrobenzyl chloride being less than that for *p*-nitrobenzyl chloride. The alternate polarity theory would lead us to expect that the chlorine in *m*-nitrobenzyl chloride should be more reactive than that in *p*-nitrobenzyl chloride. This conclusion is seen to be confirmed, not only by the velocity data, but also by the activation energy data. Applying the Bohr theory of atomic structure, it may be said that the displacement of electrons postulated by the alternate polarity theory decreases the amount of energy required to take an electron in the chlorine atom to its activated position.

Energies of Activation in Methyl Alcohol.

Base.	Benzyl chloride.	*m*-Nitrobenzyl chloride.	*p*-Nitrobenzyl chloride
Aniline	17770	17280	18030
p-Toluidine.....	17440	14480	17100
o-Toluidine	15420	14210	17680
Dimethylaniline.....	15210	13120	15960

The results described below also throw some light on the process of activation. The influence of a nitro-group in the benzyl chloride on the velocity of reaction is similar to the influence of a nitro-group in the nucleus of the amine. Also there is no evidence that, in general, the energy of activation is an additive property (Arrhenius, *Z. physikal. Chem.*, 1889, **4**, 226). It is now suggested that the formation of a loose molecular complex precedes activation and the energy of activation measured in the cases cited is the energy of activation of such a complex.

Experimental.

The method of estimation was that already described (*loc. cit.*). The constants were calculated by the modified equation, taking into account the base combined with the liberated hydrochloric acid; Moore, Somervell, and Derry (J., 1912, **101**, 2459) have already directed attention to this omission in Menschutkin's calculations and their work should have been mentioned in the previous paper.

Tertiary bases gave much more constant values of the velocity coefficient than primary; difficulty was also experienced in getting concordant results with *p*-nitrobenzyl chloride. The bases used were crystallised as their hydrochlorides or acetyl compounds in the case of primary and secondary bases. The tertiary bases were tested for freedom from primary or secondary bases by the usual acetic anhydride test. The results are tabulated below.

Velocity coefficients in methyl alcohol.

Conc. of base, 0·8*M*. Conc. of chloride, 0·2*M*.

	Temp. 45°.			Temp. 35°.		
Base.	Benzyl chloride.	*m*-Nitro-benzyl chloride.	*p*-Nitro-benzyl chloride.	Benzyl chloride.	*m*-Nitro-benzyl chloride.	*p*-Nitro-benzyl chloride.
Aniline	0·0092	0·00451	0·00365	0·00368	0·00185	0·00144
p-Toluidine.....	0·0147	0·00874	0·00667	0·00596	0·00407	0·00276
o-Toluidine ...	0·00596	0·00256	0·00207	0·00269	0·00123	0·000832
Dimethylaniline	0·00609	0·00132	0·00092	0·00278	0·000671	0·000404

Velocity coefficients at 35° and at 45°.

(*See also a preceding table*).

Conc. of benzyl chloride, 0·2*M*.

m-Toluidine : conc. 0·8*M*; $k_{35°}$ 0·00494.
m-Nitroaniline : conc. 0·8*M*; $k_{45°}$ 0·00168.
p-Nitroaniline : conc. 0·4*M*; $k_{45°} > 0·0002$.
Monomethylaniline : conc. 0·8*M*; $k_{35°}$ 0·00644; $k_{45°}$ 0·0187.
Monobenzylaniline : conc. 0·8*M*; $k_{45°}$ 0·00335.
p-Bromodimethylaniline : conc. 0·8*M*; $k_{45°}$ 0·00175.

In conclusion, I wish to thank the British Dyestuffs Corporation, Huddersfield, who supplied many of the bases used in this work, and Mr. B. K. Menon, who prepared some of the *p*-nitrobenzyl chloride.

UNIVERSITY COLLEGE, UNIVERSITY OF RANGOON,
BURMA. [*Received, April 27th* 1925.]

CCXCIV.—*A New Peroxide of Barium.*

By MARGARET CARLTON.

WHEN hydrogen peroxide is added to a well-cooled, aqueous solution of barium hydroxide, white, crystalline $BaO_2,8H_2O$ is formed. If, however, excess of hydrogen peroxide be added, the appearance of the crystals changes and a granular precipitate is formed which rapidly settles after shaking. This becomes buff-coloured on standing. If this substance be filtered off and dried in a vacuum desiccator over phosphorus pentoxide, the colour slowly darkens for a day or two, until a deep buff colour is reached; on further standing, the colour fades and a creamy powder remains. This seems to suggest the formation and decomposition of an oxide higher than BaO_2.

A study of the action of excess of hydrogen peroxide on baryta was made by Schöne (*Annalen*, 1878, **192**, 257), and he showed the existence of a white, crystalline compound, BaH_2O_4, which turned yellow on standing. He suggested that this yellow compound might be BaO_3 or BaO_4, but he did not investigate the matter further. Traube and Schulze (*Ber.*, 1921, **54**, 1626) obtained a substance which on analysis seemed to be BaO_2 with not more than 5% BaO_4.

On the suggestion of Professor Baker, I have undertaken an examination of the action of hydrogen peroxide on barium hydroxide.

A preliminary analysis of the wet substance obtained by precipitation with hydrogen peroxide was therefore carried out, by means of potassium permanganate and dilute sulphuric acid, to determine the oxygen and barium, and this indicated the presence of a substance which seemed to be almost entirely BaO_3 or BaO_4.

Fresh samples of the substance were prepared in the following way: Pure crystalline barium hydroxide (10 g.) was dissolved in 200 c.c. of water, and 10 c.c. of 30% hydrogen peroxide were slowly added with repeated shaking, the temperature of the solutions being about 15°. For the first two preparations the mixture was

kept over-night at the ordinary temperature; the following morning, the precipitate was faintly buff-coloured and was washed by decantation with cold water and finally filtered through an alundum crucible, washed again with cold water, and finally with alcohol and ether, and dried in a vacuum over phosphorus pentoxide. Later on, the substance was kept only for 10—20 minutes after the addition of the hydrogen peroxide, for the precipitate to settle; it was then washed by decantation, filtered off, and washed with water only and dried in a vacuum over phosphorus pentoxide.

Properties.—The substance is a cream-coloured, non-crystalline powder, which darkens on standing.

When it is heated gently in a dried tube, moisture collects on the walls; this does not liberate iodine from potassium iodide and therefore is not hydrogen peroxide.

On extracting with ether and testing the extract for hydrogen peroxide, no trace was found, showing the absence of free hydrogen peroxide and also of hydrogen peroxide of crystallisation.

The solid substance decolorises neutral potassium permanganate more rapidly than barium dioxide, giving a brown colour and evolution of oxygen.

It does not liberate iodine from neutral potassium iodide even on standing, but when a few drops of dilute nitric acid are added, iodine is rapidly liberated; more iodine separates than from a similar amount of barium dioxide.

With neutral potassium bromide there is no action but on acidifying with a few drops of either nitric or hydrofluoric acid, bromine is freely liberated, whereas only a trace of bromine is produced from barium dioxide.

With strong hydrochloric acid, there is a vigorous action and chlorine is liberated freely; with barium dioxide only a trace of chlorine is produced.

When it is heated with flowers of sulphur a very vigorous action takes place; a peculiar odour is observed afterwards but no sulphur dioxide (compare barium dioxide, where there is a fairly vigorous action with formation of sulphur dioxide).

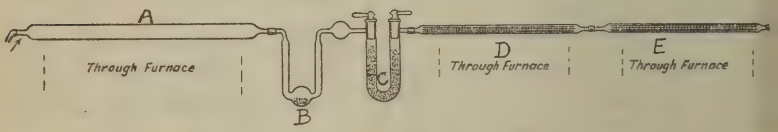
The foregoing tests show the presence of a very vigorous oxidising agent, and attempts to determine the amount of oxygen in the compound were made. Analyses had to be carried out before the substance was completely dry, owing to its instability. The oxide was only dried for about an hour over phosphorus pentoxide, in a vacuum; the first sample was then taken for analysis. Two analyses were made at the same time, by different methods. The first analysis consisted in determining the oxygen and water given off when the substance was heated in an atmosphere of

nitrogen. The apparatus used is shown in the accompanying sketch.

A weighed amount of the substance (1—2 g.) was introduced into a weighed Jena glass bulb, B. This was connected through a ground joint to a U-tube, C, containing calcium chloride and to the two tubes, D and E, containing freshly-reduced copper gauze. The tubes C, D, and E were weighed before and after each experiment.

Nitrogen, from which traces of oxygen were removed by passage over the heated tube, A, of copper, was slowly passed through the apparatus and when all the air had been displaced, the tubes, D and E, containing the copper gauze, were heated by means of electric furnaces to 500—600°. When these were hot, the bulb B was heated in a water-bath until the whole of the water in the oxide appeared to have been removed. This sometimes took as long as 3 hours; the bath was then removed and the bulb gently heated nearly to dull redness for a few minutes. The bulb was then allowed to cool; when it was cold, the furnaces heating D

Fig. 1.



and E were switched off and the whole apparatus was left to cool with the nitrogen bubbling through. When cold, the nitrogen was displaced by a slow current of dry air and the tubes C, D, and E and the bulb B were weighed.

The formula was calculated on the assumption that the residue was barium dioxide. This was found not always to be the case; barium dioxide decomposes somewhat when heated in a vacuum to 450° and, since the partial pressure of oxygen is here very small, possibly the same effect is produced and the proportion of oxygen calculated in this way may be rather high.

The weight of water collected in C was subtracted from the actual weight of oxide taken, to give the amount of anhydrous salt used in each experiment. The values of x in BaO_x are given in the table.

The second analysis of the substance was performed while the analysis described above was being carried out. A second sample of the oxide was examined for available oxygen and for barium.

A weighed amount of the salt, dissolved in dilute nitric acid, was titrated with potassium permanganate; the barium was then precipitated from the same solution and weighed as barium sulphate.

This gave an independent estimate of the barium and oxygen present.

The equation used in calculating the composition of the substance is :—

$$BaO_x + \tfrac{2}{5}(x-1)KMnO_4 + \{\tfrac{3}{5}(x-1)+1\}H_2SO_4 = BaSO_4 + \frac{x-1}{5}K_2SO_4 + \tfrac{2}{5}(x-1)MnSO_4 + \{\tfrac{3}{5}(x-1)+1\}H_2O + (x-1)O_2.$$

From which we get that 137 g. of barium correspond to $\frac{2}{5}(x-1)16$ g. of oxygen. And so the value of x can be calculated.

The results are given in the table.

Owing to the uncertainty as to the decomposition of the barium dioxide, a second method was used in liberating oxygen from the compound. Instead of heating the BaO_x in an atmosphere of nitrogen, the air was displaced from the apparatus as before and the weighed tubes containing the copper were heated, then a slow current of carbon dioxide was passed and the oxide heated as before; the residue was obtained as barium carbonate, which is quite stable at the temperature used.

Interval between preparation and analysis.	Value of x from dry analysis.	Value of x from wet analysis.	Interval between preparation and analysis.	Value of x from dry analysis.	Value of x from wet analysis.
About 4 hours	—	2·91	2 days	2·85	2·87
2 days	3·7	2·86	4 days	2·56	—
6 days	—	2·4		3·07	3·3*
immediately	—	2·91	Washed with water only.		
1 day	2·42	2·89	same day	2·99	—
1 day	3·04	2·99	1 day	2·68	2·87
3 days	2·73	2·55	same day	3·26	2·98
same day	3·91	2·9	same day	3·7	2·96
1 day	3·4	2·79	2 days	3·14	2·74
1 day	2·9	2·79		3·37	2·9
1 day	2·99	2·90	Residue obtained as barium carbonate.		
2 days	3·2	—	same day	2·89	2·71
3 days	2·8	2·63	1 day	2·83	—
			same day	2·77	—
			same day	2·96	3·21

Results bracketed together are different analyses of the same preparation.

* The preparation and determination of this sample were kindly carried out by Mrs. Muriel Baker.

Conclusion.

(1) By the action of an excess of hydrogen peroxide on barium hydroxide at temperatures below 20° a new substance is formed.

(2) This substance is unstable and is a vigorous oxidising agent, being much more reactive than barium dioxide, *e.g.*, liberates bromine from potassium bromide and chlorine very freely from hydrogen chloride.

(3) The results of analysis indicate that it probably has the formula BaO_3.

It is proposed to use this substance in an attempt to prepare a new peroxide of hydrogen. The work will be done in conjunction with Professor Baker and Mrs. Baker, repeating and extending experiments which they have already made with potassium tetroxide.

I wish to express my thanks to Professor Baker for his kind help and encouragement in this research.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, July 4th*, 1925.]

CCXCV.—*The Action of Aldehydes on the Grignard Reagent. Part III.*

By JOSEPH MARSHALL.

ONLY when an aldehyde in less than one molecular proportion is allowed to react with an ethereal solution of a magnesium alkyl halide is the expected secondary carbinol the chief product of the reaction; if an excess is added, almost the whole of the excess is combined in some manner with the magnesium complex and the product obtained on decomposition of the mass with water is a mixture containing as one of its constituents the primary alcohol corresponding to the aldehyde used in the reaction (J., 1914, **105**, 527; 1915, **107**, 509). Papers recently published (Meisenheimer, *Annalen*, 1925, **442**, 180; Hess, *Annalen*, 1924, **437**, 256; Rheinboldt, *J. pr. Chem.*, 1925, **109**, 175) agree with the results of the author up to this point, but they differ both as to the mechanism by which the alcohol is supposed to be formed in the reaction and also as to the nature of the other products. Meisenheimer and Hess, whilst not in accord in detail, both suggest that the original co-ordination compound of magnesium ethyl bromide and benzaldehyde is capable of resolution in two directions indicated by the schemes :—

$$\text{(1) PhCHEt·OMgBr} \longleftarrow \text{PhCHO} + \text{MgEtBr} \longrightarrow \text{PhCH}_2\text{·OMgBr} + \text{C}_2\text{H}_4 \quad \text{(2)}$$

the second of these resolutions taking place to a much smaller extent than the first.

The reduction of the aldehyde is represented by this theory as being due to the addition of a hydrogen atom from the alkyl halide, and hence the alkylene evolved should be equivalent to the alcohol

produced. Meisenheimer points out that he has never observed this equivalence, but suggests that some isomerisation takes place.

When an aryl halide is used in the reaction, the author has shown that a primary alcohol is again formed. The scheme representing this would appear to be

$$PhCHO + MgPhBr \longrightarrow PhCH_2{\cdot}OMgBr + C_6H_4< \quad . \quad (3)$$

and this might reasonably be expected to result in the production of diphenylene, which, however, has never been observed in this reaction.

This theory does not explain the production of substances in the Grignard reaction under discussion other than the secondary alcohol, which is the normal product, and the primary alcohol corresponding to the aldehyde used in the reaction; the presence of any other compounds in the product of the reaction would entail a considerable extension of the theory.

The author (*loc. cit.*) showed that along with the primary and secondary alcohols obtained in a Grignard reaction the ketone corresponding to the secondary alcohol is formed, with condensation products of this ketone and the aldehyde used in the reaction. Thus, when benzaldehyde in excess reacts with magnesium methyl iodide, the products which may be isolated are benzyl alcohol, acetophenone, phenyl styryl ketone, and dibenzoylmethane, while the phenylmethylcarbinol which, normally, would be the main product of the reaction is almost entirely absent. Again, when benzaldehyde in excess reacts with magnesium phenyl bromide, the only products are benzyl alcohol and benzophenone, whilst with magnesium benzyl bromide, benzaldehyde produces, besides benzyl alcohol and deoxybenzoin, a large amount of phenyldibenzoylmethane.

The suggestion was hazarded in one of the earlier papers that the new reaction was analogous to Cannizzaro's reaction, in which one molecule of benzaldehyde oxidises a second molecule of the same aldehyde to benzoic acid, being itself reduced to benzyl alcohol. If this suggestion be correct, it is evident that when cinnamaldehyde is allowed to react with magnesium ethyl iodide as described by Meisenheimer, there is the possibility of the formation of styryl ethyl ketone and other condensation products along with cinnamyl alcohol and styrylethylcarbinol.

Since styryl methyl ketone is more easily identified than the ethyl compound, the experiment was first carried out with magnesium methyl iodide, with the result that whilst styryl methyl ketone was isolated as the phenylhydrazone in good yield, the only alcohol which could be obtained was cinnamyl alcohol. This was isolated

as the *p*-nitrobenzoyl ester (m. p. 76°; compare Meisenheimer, *loc. cit.*) and there was no indication of the presence of styrylmethylcarbinol either as its ester or as phenylbutadiene, which might have been formed as phenylpentadiene is produced when *p*-nitrobenzoyl chloride acts on styrylethylcarbinol. The corresponding reaction with magnesium ethyl iodide was performed with results similar to those obtained with magnesium methyl iodide, but in this case, by longer boiling of the reaction product, an attempt was made to secure the formation of more complicated products.

Since it has been shown in earlier papers that alkyl aldehydes are capable of reacting in a manner analogous to that in which aromatic aldehydes react, it was of interest to determine whether the simplest aldehyde, formaldehyde, would react similarly. The normal product of this reaction is the primary alcohol (*Compt. rend.*, 1902, **134**, 107), and it would be expected that excess of formaldehyde would oxidise part at any rate of the primary alcohol to the aldehyde. Accordingly, the reaction between magnesium phenyl bromide and trioxymethylene was investigated, with the result that a considerable quantity of benzaldehyde was isolated, although the chief product of the reaction was benzyl bromide (compare J., 1914, **105**, 534).

Experimental.

Action of Cinnamaldehyde on Magnesium Methyl Iodide.—An ethereal solution of cinnamaldehyde (132 g.; 1 mol.) was added to the Grignard solution prepared from magnesium powder (24 g.; 1 mol.) and methyl iodide (142 g.; 1 mol.), cooled in a freezing mixture. At first a yellow precipitate formed which immediately dissolved on shaking, but when about half the aldehyde had been added a greyish-white solid began to separate. Three hours later, a second molecule of cinnamaldehyde in ether was added quickly, whereby the precipitate was changed into a viscous, yellowish-brown material. After 12 hours, the mixture was heated on the steam-bath during 10 hours and cooled, and the ether was poured into ice and hydrochloric acid, separated, and shaken with sodium bisulphite solution, when about 2 g. of the bisulphite compound of cinnamaldehyde separated. From the residual ether 2 g. of a dark-coloured, sticky material was obtained which was not examined.

The heavy, yellow mass from which the ether had been poured was shaken with ice and hydrochloric acid and a further quantity of ether until solution was effected. The ethereal extract was shaken several times with concentrated bisulphite solution, and 20 g. of cinnamaldehyde bisulphite compound were obtained corresponding to about half this weight of aldehyde. The ether was washed with

sodium carbonate solution and from this, 4 g. of cinnamic acid were isolated. The ether was now evaporated and the residue distilled in a vacuum. A fraction (165 g.) was obtained, b. p. 150—180°/15 mm., while a second fraction (20 g.) distilled at 220—260°. As this did not crystallise, it was not examined; heat was developed when it was mixed with phenylhydrazine. The main fraction was cooled in a freezing mixture and inoculated with a crystal of styryl methyl ketone. The crystals produced could not be isolated owing to the rapidity with which fusion occurred. The whole of the material was dissolved in alcohol and warmed with phenylhydrazine (80 g.) during 2 hours on the water-bath. The yellow crystals which had separated after 12 hours melted at 158° after being washed with alcohol (yield 100 g.). The mother-liquor was evaporated, and after removal of a second crop of crystals, the thick residue was poured into water, washed with dilute hydrochloric acid, separated from the acid, and steam-distilled. The product in the distillate was extracted with ether and, after removal of the ether, was treated with *p*-nitrobenzoyl chloride in pyridine solution. Addition of water precipitated an oil which immediately solidified and, after recrystallisation from alcohol, the compound melted at 76°. It was compared with and found identical with the corresponding ester of cinnamyl alcohol.

The phenylhydrazone (m. p. 158°) was compared with that obtained from styryl methyl ketone and the identity of the two compounds was proved. After heating in a vacuum, and subsequent distillation, both boiled at 245—250°, and the distillate in each case solidified, yielding, after recrystallisation from spirit, white, crystalline prisms, m. p. 113°, and giving with a nitrite solution the magenta colour which is characteristic of 1 : 5-diphenyl-3-methylpyrazoline.

Action of Cinnamaldehyde on Magnesium Ethyl Iodide.—Magnesium (24 g.; 1 mol.) and ethyl iodide (156 g.; 1 mol.) were allowed to react in anhydrous ether with cooling, and cinnamaldehyde (264 g.; 2 mols.) added as in the experiment with methyl iodide. A brownish-yellow mass was again obtained which was heated during 20 hours on the steam-bath and then decomposed with ice and hydrochloric acid; a bright orange, crystalline material (20 g.) not very soluble in ether then separated which melted at 158° after recrystallisation from spirit and has not yet been identified.

After the ether solution had been washed with bisulphite solution, the ether was removed and the residue thoroughly steam-distilled. From the distillate was extracted an oil, of which a quantity was allowed to react with half its weight of phenylhydrazine. Evolution of heat occurred and after cooling the addition of a little spirit induced the crystallisation of the phenylhydrazone, m. p. 102°, of styryl ethyl ketone. From a second part of the oil cinnamyl

p-nitrobenzoate was obtained by the action of *p*-nitrobenzoyl chloride in pyridine solution.

Action of Trioxymethylene on Magnesium Phenyl Bromide.—The Grignard reagent prepared from bromobenzene (157 g.; 1 mol.) (after separating from unchanged metal) was boiled with trioxymethylene (60 g.; 2 mols.) for 48 hours, a brownish-yellow, viscous mass forming. After decomposition of this material with dilute acid the ethereal extract was shaken with sodium bisulphite solution, 20 g. of the bisulphite compound of benzaldehyde were filtered off, and the ethereal solution remaining was fractionated, 35 g. of benzyl bromide and about 10 g. of diphenyl being obtained.

The author desires to thank the Directors of Boots Pure Drug Co., Ltd., for permission to carry out this work in their laboratories and for the assistance of the Analytical Department of the firm in the analysis of the products obtained.

BOOTS PURE DRUG CO., LTD.,
NOTTINGHAM.

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CCXCVI.—*Optical Activity and the Polarity of Substituent Groups. Part II. Menthyl Esters of Substituted Acetic Acids.*

By HAROLD GORDON RULE and JOHN SMITH.

POLARITY as applied to substituent effect has, at the present time, at least two distinct meanings in chemistry. On the one hand it is used in the phrase, *general polar effect*, in connexion with a series such as

$$NO_2,\ CN,\ CO_2H,\ Cl,\ Br,\ I,\ OMe,\ H,\ Me,$$

representing the relative influence of the groups on the acidic strength of an aliphatic acid. This sequence has also been traced in the effect of the substituents on velocity of reaction and molecular inductive capacity (see Rule and Paterson, J., 1924, **125**, 2155).

On the other hand, groups are frequently described as positive and negative, either in reference to their directive influence on benzene substitution (Vorländer), or by deduction from Lapworth's principle of induced alternate polarities, or from the electronic theory. On this last basis, it has been shown (Rule, J., 1924, **125**, 1121) that the polarity of substituents, as deduced from the views of J. J. Thomson, leads to the *polar series*

$$NO_2,\ CN,\ CO_2H,\ H,\ Me,\ I,\ Br,\ Cl,\ F,$$

and that this closely corresponds to the relative influence of the

groups on the nitration of benzene, and also on the optical activity of the menthyl esters of *o*-substituted benzoic acids and of certain derivatives of amyl alcohol. Hence the suggestion was advanced that, in general, positive and negative groups influence the rotation of a parent compound in opposite directions, in accordance with the polar series above. The optical activity of other series of compounds was also quoted in support of this suggestion, but very little definite evidence relating to positive groups could be obtained.

In investigations summarised in *Gazzetta*, 1923, **53**, 417, Betti has determined the rotatory powers of a large number of products prepared by condensing an active base with substituted benzaldehydes, with results which show a remarkably close agreement between rotatory powers and the dissociation constants of the corresponding benzoic acids. The measurements, however, all referred to the one solvent, benzene, and to light of one wave-length. Only one positive group (NO_2) is included in the list of substituents examined by Betti, and it is known that solvents may exert a marked preferential effect on the rotation of compounds containing certain substituents, as is seen from the abnormally high rotation of menthyl *o*-nitrobenzoate in benzene solution (Cohen and Armes, J., 1905, **87**, 1190).

In the present communication are recorded the rotatory powers of menthyl esters of the acids $CH_2X{\cdot}CO_2H$, where X = CN,* CO_2H, OH, OMe, and OEt. Determinations were carried out at temperatures between 20° and 95° with the compounds in the homogeneous state, where feasible, and for light of four wave-lengths.

Discussion of Results.

In all cases it was found that the observed rotations could be expressed within the limits of experimental accuracy by a Drude equation of one term. It appears, therefore, that the dispersion is in every case normal and simple. The values of the optical constants and of the dispersion ratio, α_{gr}/α_D, obtained for the acetic derivatives are summarised in Tables I and II.

It will be seen that the substituents affect the rotatory power in the order $CN > OH > OMe > OEt > CO_2H$ and that the values undergo little change with temperature. The values of λ_0^2 vary between 0·0238 and 0·0316 for the homogeneous esters. A number of observations were also made with cyanoacetic ester, glycollic ester, and the hydrogen malonic ester in benzene and chloroform solution. In these cases also the dispersion was apparently simple in character.

* The rotatory power of menthyl cyanoacetate in benzene solution for the D line has been determined by Lapworth (J., 1904, **85**, 43).

Table I.

l-*Menthyl Esters of Acids* $CH_2X{\cdot}CO_2H$ (*Homogeneous State*).

(All rotations are negative in sign.)

X.	CO_2H.		OEt.			
Temp.	59·5°	90·5°	20·5°	37°	61·3°	93·7°
$[K]$	20·72	20·47	21·30	21·39	21·55	21·60
λ_0^2	0·0316	0·0309	0·0262	0·0261	0·0261	0·0269
α_{gr}/α_D	1·184	1·184	1·180	1·182	1·181	1·183
$[M]_D$	158·8°	157·6°	160·6°	161·1°	161·9°	162·9°

X.	OMe.				OH.	CN.
Temp.	20·5°	34·5°	55·5°	93·7°	94·3°	91·3°
$]K]$	23·16	22·95	22·89	22·94	24·34	25·25
λ_0^2	0·0273	0·0278	0·0286	0·0274	0·0312	0·0238
α_{gr}/α_D	1·182	1·181	1·183	1·183	1·184	1·179
$[M]_D$	165·0°	164·4°	163·7°	162·8°	165°	174·1°

Table II.

In Solution (5% *concentration*).*

(All rotations are negative in sign.)

X.	CO_2H.	OH.		CN.	
Solvent.	Benzene.	Benzene.	Chloroform.	Benzene.	Chloroform.
Temp.	18·6°	17·6°	12·3°	19·2°	21·6°
$[K]$	20·14	24·27	26·46	26·20	26·34
λ_0^2	0·0276	0·0255	0·0257	0·0198	0·0334
α_{gr}/α_D	1·185	1·185	1·185	1·181	1·187
$[M]_D$	155·1°	161·2°	180·1°	178·3°	186·9°

* For other concentrations, see Experimental section.

The values of the ratio α_{gr}/α_D for the homogeneous and dissolved compounds remain very constant in the neighbourhood of 1·182.

When the above molecular rotations are compared with rotations recorded in the literature for menthyl esters of other mono-substituted acetic acids, and arranged in order of increasing values, we obtain the following list:

X.	H.	CO_2H.		Me.	OEt.		OMe.		OH.	Br.	Cl.	CN.
$[M]_D$	−157°	158·8°	157·6°	160·2°	160·6°	162·8°	165·0°	162·9°	165·6°	169°	171°	174·1°
Temp.°	*	59·5	90·5	*	*	90	*	90	94·3	*	*	91·3

* Room temperature.

The relative effect of the substituents on optical activity in this case is therefore,

I. $CN > Cl > Br > OH > OMe > OEt > Me > CO_2H > H.$

This corresponds closely with the general polar effect of the groups, as may be seen by comparison with series II, representing

their influence on molecular inductive capacity (see Rule and Paterson, *loc. cit.*), and with series III, representing their influence on the acidity of acetic acid.

II. $CN > CO_2H(?) > OH > Cl > Br > (OMe,OEt) > CO_2H(?) > Me > H$.
III. $CN > CO_2H > Cl > Br > OMe > OH > H > Me$.

The position of the carboxyl group in series II is somewhat doubtful, formic acid having a high inductive capacity and acetic and propionic acids low values.

The analogy between the effect of substitution on optical activity and acidic strength which has previously been drawn by Betti (*loc. cit.*) is therefore confirmed and amplified. Among the menthyl esters of acetic acid there is no indication of positive groups affecting the rotatory power in an opposite sense to negative groups, as is the case with the benzoates.

It may therefore be concluded that the two types of group effect previously observed, namely, the general effect visible in inductive capacity, acidic strength and chemical reactivity, and the polar effect, as deduced from the electronic theory and traceable in benzene substitution and electromagnetic rotation, are both to be found in optical activity.

Experimental.

The menthol used was specially purified material, with a rotation of $[\alpha]_D^{18^\circ}$ $-49{\cdot}50^\circ$ in 5% ethyl-alcoholic solution.

The ethoxy- and methoxy-acetic esters were prepared by the method described in U.S. Pat. 836914, and D.R.-P. 191547, in which, however, no mention is made of rotatory power.

l-*Menthyl methoxyacetate* was prepared from the corresponding acid chloride, menthol and pyridine, in benzene solution. On being fractionated under reduced pressure, it was obtained as a colourless, odourless liquid, b. p. 141°/16 mm. After the second fractionation, a repetition of the process produced no change in rotatory power. It has not previously been recorded that *l*-menthyl methoxyacetate is a solid of m. p. 18° (Found: C, 68·4; H, 10·45. Calc. for $C_{13}H_{24}O_3$, C, 68·4; H, 10·5%).

l-*Menthyl ethoxyacetate*, prepared in a similar way, boiled at 150°/18 mm. It also was odourless (Found: C, 69·4; H, 10·7. $C_{14}H_{26}O_3$ requires C, 69·4; H, 10·7%).

l-*Menthyl glycollate* is also described in the same brief manner in the patent specification, D.R.-P. 136411. It was prepared by heating glycollic acid (3 mols.) with menthol (1 mol.) on a steam-bath for 14 hours, dry hydrogen chloride being passed through

the mixture for 10 minutes in each hour. The cooled mass was extracted with ether, washed, and dried. After removal of ether, the menthol was distilled under diminished pressure (oil-bath at 130°). The resulting dark solid was finally recrystallised from light petroleum until of constant rotation. The pure ester crystallises in long, white needles, m. p. 87·5° (above specification quotes 87°). It is moderately soluble in benzene and readily soluble in chloroform (Found: C, 67·3; H, 10·3. Calc. for $C_{12}H_{22}O_3$, C, 67·3; H, 10·3%).

l-*Menthyl cyanoacetate* was obtained from ethyl cyanoacetate by the method of Lapworth (*loc. cit.*).

l-*Menthyl Hydrogen Malonate.*—Dimenthyl malonate was first prepared by a modification of the method of Hilditch (J., 1909, **95**, 1571), using, however, pyridine as condensing agent.

The pure diester had a rotation of $\alpha^{20°}_{5461} = -9·36°$ (4·98% chloroform solution; $l = 2$). Hall (J., 1923, **123**, 109) quotes −9·32°.

In the preparation of menthyl hydrogen malonate, the diester (22 g.), dissolved in 96% alcohol (1 litre), was hydrolysed at 0° by gradual addition of the requisite amount of sodium ethoxide in alcoholic solution. On recrystallisation from ethyl acetate, it was obtained in plates, m. p. 58·5—59° (Found: C, 64·4; H, 9·1. $C_{13}H_{22}O_4$ requires C, 64·5; H, 9·1%).

Densities and Rotatory Powers of the Esters in the Homogeneous State.

Rotations generally refer to a 50 mm. tube (* indicates 100 mm.) and are all negative in sign.

l-Menthyl methoxyacetate.

$D^{t°}_{4°}$	1·0136 at 20°; 0·9964 at 40·3°; 0·9807 at 60°; 0·9638 at 80°.
α_D	73·33°* at 20·5°; 72·07°* at 34·5°; 35·31° at 55·5°; 34·13° at 93·7°.
α_{ye}	76·47°* at 20·5°; 75·14°* at 34·5°; 36·82° at 55·5°; 35·65° at 93·7°.
α_{gr}	86·70°* at 20·5°; 85·14°* at 34·5°; 41·78° at 55·5°; 40·40° at 93·7°.
α_{vl}	144·32°* at 20·5°; 142·02°* at 34·5°; 69·74° at 55·5°; 67·19° at 93·7°.

l-Menthyl ethoxyacetate.

$D^{t°}_{4°}$	0·9545 at 20°; 0·9379 at 40·6°; 0·9242 at 58°; 0·9070 at 79·2°.
α_D	63·31°* at 20·5°; 31·31° at 37°; 30·89° at 61·3°; 30·16° at 93·7°.
α_{ye}	65·96°* at 20·5°; 32·70° at 37°; 32·28° at 61·3°; 31·50° at 93·7°.
α_{gr}	74·68°* at 20·5°; 37·01° at 37°; 36·48° at 61·3°; 35·70° at 93·7°.
α_{vl}	124·18°* at 20·5°; 61·41° at 37°; 60·57° at 61·3°; 59·31° at 93·7°.

l-Menthyl glycollate.

$D^{t°}_{4°}$ 0·9469 at 94·3°.

At 94·3° $\alpha_D = 36·50°$; $\alpha_{ye} = 38·09°$; $\alpha_{gr} = 43·23°$; $\alpha_{vl} = 72·71°$.

l-Menthyl cyanoacetate.

$D^{t°}_{4°}$ 0·9406 at 91·3°.

At 91·3° $\alpha_D = 36·71°$; $\alpha_{ye} = 38·28°$; $\alpha_{gr} = 43·28°$; α_{vl} (not determined owing to slight yellow colour of liquid).

l-Menthyl hydrogen malonate.

$D_{4^\circ}^{t^\circ}$ 1·0238 at 59·5°; 1·0008 at 90·5°.

At 59·5° $\alpha_D = 33{\cdot}61°$; $\alpha_{ye} = 35{\cdot}07°$; $\alpha_{gr} = 39{\cdot}89°$; $\alpha_{vi} = 67{\cdot}01°$.

At 90·5° $\alpha_D = 32{\cdot}60°$; $\alpha_{ye} = 33{\cdot}96°$; $\alpha_{gr} = 38{\cdot}59°$; $\alpha_{vi} = 64{\cdot}86°$.

Rotatory Powers of the Esters in Solution.

Ester.	Solvent.	Temp.	G. of ester in 100 c.c.	α obs. (*l* = 2). α_D.	α_{ye}.	α_{gr}.	α_{vi}.
Glycollate	Benzene	17·6°	5·004	7·54°	7·89°	8·94°	14·76°
,,	Chloroform	12·3	5·003	8·42	8·77	9·98	16·49
,,	,,	12·3	16·192	27·06	—	—	—
Cyanoacetate	Benzene	19·2	5·002	8·00	8·38	9·45	15·40
,,	,,	17·0	11·36	4·51	(50 mm. tube)		
,,	Chloroform	21·8	5·004	8·39	8·81	9·96	16·83
,,	,,	21·0	14·981	6·21	(50 mm. tube)		
Hydrogen malonate	Benzene	18·8	4·914	6·30	6·56	7·47	12·41
,, ,,	,,	19·0	20·08	12·88	(1 dcm. tube)		

Specific Rotatory Powers of Esters in Homogeneous State.

l-Menthyl methoxyacetate.

t.	$D_{4^\circ}^{t^\circ}$.	$[\alpha]_D$.	$[\alpha]_{ye}$.	$[\alpha]_{gr}$.	$[\alpha]_{vi}$.
20°	1·0136	−72·35°	−75·49°	−85·56°	−142·39°
40	0·9970	72·04	74·92	84·93	141·95
60	0·9805	71·72	74·78	84·89	141·68
80	0·9638	71·63	74·83	84·87	141·32
90	0·9555	71·47	74·87	84·87	141·14

l-Menthyl ethoxyacetate.

20	0·9545	−66·35	−69·10	−78·29	−130·20
40	0·9383	66·62	69·62	78·76	130·66
60	0·9224	66·90	70·05	79·18	131·37
80	0·9063	67·19	70·30	79·54	132·05
90	0·8983	67·30	70·35	79·69	132·38

	t.	$D_{4^\circ}^{t^\circ}$.	$[\alpha]_D$.	$[\alpha]_{ye}$.	$[\alpha]_{gr}$.	$[\alpha]_{vi}$.
l-Menthyl hydroxyacetate	94·3°	0·9469	−77·09°	−80·48°	−91·26°	−153·6°
cyanoacetate	91·3	0·9406	78·06	81·39	92·03	—
hydrogen malonate	59·5	1·0238	65·65	68·51	77·75	130·9
,, ,,	90·5	1·0008	65·14	67·86	77·11	129·6

Specific Rotatory Powers of l*-Menthyl Esters in Solution.*

Ester.	Solvent.	G. of ester in 100 c.c.	Temp.	$[\alpha]_D$.	$[\alpha]_{ye}$.	$[\alpha]_{gr}$.	$[\alpha]_{vi}$.
Glycollate	Benzene	5·004	17·6°	75·34°	78·84°	89·33°	147·5°
,,	Chloroform	5·003	12·3	84·15	87·64	99·74	164·8
Cyanoacetate	Benzene	5·002	19·2	79·97	83·77	94·46	153·9
		11·365	17·0	79·37			
,,	Chloroform	5·004	21·8	83·83	88·03	99·52	168·2
		14·981	21·0	82·91			
Hydrogen malonate	Benzene	4·914	18·8	64·10	66·74	76·00	126·3
		20·078	19·0	64·14			

Molecular Rotations of Esters.

Substituent group.	Temp.	Mol. rotations. Liq. state.	Mol. rotations. Solution.	Substituent group.	Temp.	Mol. rotations. Liq. state.	Mol. rotations. Solution.
CO_2H	18·8°	—	155·1°*	OMe	60°	163·5°	
	59·5	158·8°			80	163·3	
	90·5	157·6			90	162·9	
OEt	20	160·6		OH	12·3	—	180·1†
	40	161·2			17·6	—	161·2*
	60	161·9			94·3	165·0	
	80	162·6		CN	19·2	—	178·3*
	90	162·8			21·8	—	186·9†
OMe	20	165·0			91·3	174·1	
	40	164·2					

Solvent: * benzene, † chloroform.

In conclusion, the authors desire to thank the Earl of Moray Fund for a grant which has covered most of the expenses involved.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF EDINBURGH. [*Received, July 4th,* 1925.]

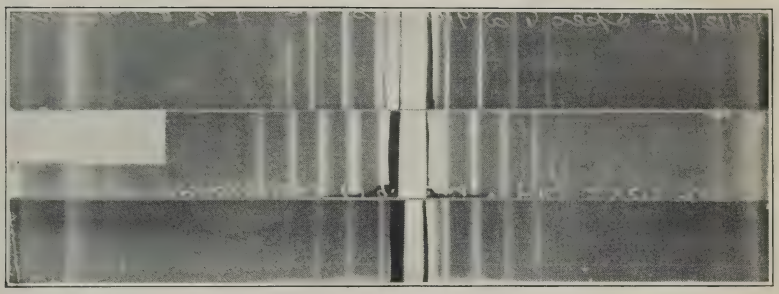
CCXCVII.—X-*Rays and the Constitution of the Hydrocarbons from Paraffin Wax.*

By STEPHEN HARVEY PIPER, DENNIS BROWN, and STANLEY DYMENT.

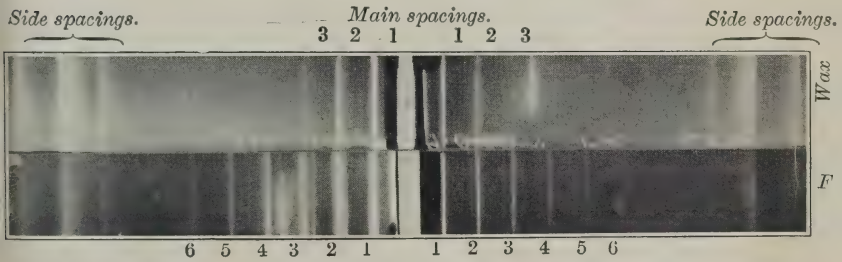
SINCE the distance apart of the main cleavage planes of the crystals of long-chain compounds has a definite relation to the length of the constituent molecules (Müller and Shearer, J., 1923, **123**, 2043, 3153; this vol., pp. 592, 600), *X*-ray examination of the spacing of such planes of unknown crystals may give important information as to the nature of the structural molecules. The nature of the hydrocarbons composing paraffin wax is unknown, although it has been conjectured, on slender evidence, that they are higher members of the normal methane series. It was hoped that *X*-ray examination of the crystals of the individual hydrocarbons would throw some light on their constitution.

Origin of the Hydrocarbons.—The seven solid hydrocarbons, an investigation of which forms the subject of this communication, were isolated by Prof. Francis and his students from Scotch paraffin wax by long-continued fractionation in high vacua (J., 1922, **121**, 1529). These authors believed that 80% of the original material was composed of seven hydrocarbons, boiling at constant temperature; and their opinion that these hydrocarbons were not mixtures was strengthened by their later work (*loc. cit.*, p. 2804), which showed

FIG. 1.



* *Dotriacontane.*



[*To face p.* 2194.]

that, on oxidation of each fraction by air, the small amounts of hydrocarbon which escaped this process were identical in every case with the original material.

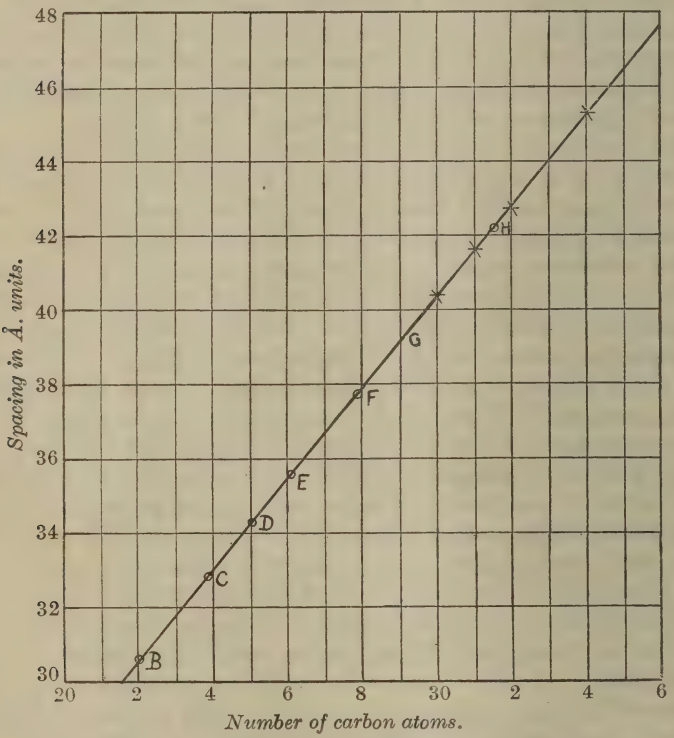
Krafft (*Ber.*, 1907, **40**, 4779) isolated eighteen hydrocarbons by fractionation of Saxon paraffin wax in the " vacuum of the cathode rays," and identifying these with those he had synthesised from materials of known constitution, drew the conclusion that the wax was composed of a large number of the higher normal members of the paraffin hydrocarbons. Francis has pointed out, however, that five fractionations of such a complex mixture were quite insufficient to indicate the presence of constant-boiling substances, that pure hydrocarbons could not have been isolated, and hence no satisfactory deduction could be drawn from a comparison between these impure substances and synthetic normal hydrocarbons.

The seven solid hydrocarbons obtained by Francis, and here lettered B to H in ascending order of melting points, appeared to differ in some respects from normal hydrocarbons, and it seemed possible that *X*-rays might show if they varied in crystalline form.

The substances were melted on glass strips, and the reflection spectra yielded by iron *K*-rays from a Shearer tube were photographed on a Müller spectrograph. All the specimens gave good photographs, some of which are reproduced in Fig. 1. All showed one set of planes with a large spacing, and two or three smaller " side spacings." These side spacings were the same for all the substances examined, but the large spacings increased with molecular weight and the appearance of the plates suggested that they belonged to a series of some kind. For the sake of comparison, synthetic triacontane, dotriacontane, and tetratriacontane were photographed. The main spacings measured for these substances are plotted in Fig. 2 against the number of carbon atoms they contain, and the spacings obtained from the unknown hydrocarbons isolated from paraffin wax have been set out on the straight line drawn through these points. It will be seen that, with the exception of H, each hydrocarbon spacing agrees almost exactly with a whole number of carbon atoms, and this number we consider to be the number of carbon atoms in the substance. The number of carbon atoms so obtained does not, however, in the cases of B, E, F, and G agree with the value deduced from the molecular weight determinations and published by Francis (J., 1922, **121**, 1531). In Table I, columns 3 and 4, the two sets of values are compared. We considered that our graph showed definitely the presence of the seven different hydrocarbons in column 3, and our belief in the method was strengthened by a measurement made on a hydrocarbon synthesised by the electrolysis of what was believed to be pure stearic acid, and which

therefore should have been tetratriacontane. The photograph of this hydrocarbon, however, only showed the lines corresponding to dotriacontane, and further examination proved that the specimen actually was this hydrocarbon. An investigation of the stearic acid used in the preparation showed the presence of a quantity of palmitic acid; consequently the reaction must have taken place between the radicals of palmitic and stearic acids rather than of stearic acid only. A specimen of a hydrocarbon prepared by the

FIG. 2.



× *Synthetic hydrocarbons.* ○ *Hydrocarbons from paraffin wax.*

same method from carefully purified stearic acid gave the spacing expected for tetratriacontane. A redetermination of the molecular weights of the hydrocarbons from the paraffin wax was obviously desirable, and this was undertaken by Dr. Christie of the Chemical Department, to whom our best thanks are due.

The difficulty of obtaining trustworthy results by the Beckmann ebullioscopic method is well known, in spite of the fact that, a definite experimental procedure always being adopted, very

concordant observations may be made. Using benzene as a solvent, Prof. Francis (*loc. cit.*) had obtained data agreeing among themselves in many cases to 1%. In order to vary the procedure, Dr. Christie employed the newer method of Menzies and Wright (*J. Amer. Chem. Soc.*, 1921, **43**, 2314), which is stated by these authors to give more accurate results. The constant for benzene, 26·1, given by them gave too low a value for the molecular weight of dotriacontane, which was regarded as a standard; the value 26·67 has therefore been used throughout these determinations, which in all cases were carried out under precisely similar conditions.

The mean molecular weight determined for dotriacontane was 452 in both chloroform and benzene. The calculated value is 450 and in each solvent individual determinations did not differ by as much as 1%.

Fraction B. The old value 325 was confirmed, four determinations in benzene giving 321 with a maximum variation of just over 1%. $C_{23}H_{48}$ requires *M*, 324.

Fraction C. The previous value was 332. Using benzene as a solvent, the mean of eight determinations by the new method was found to be 336 with an extreme variation of just under 2%. In chloroform the mean of seven determinations gave 338 with a variation of about 1%. $C_{24}H_{50}$ requires *M*, 338.

Fraction D. Only a small quantity of this fraction was available. The old value was 358, but in benzene *M* was now found to be distinctly higher, *viz.*, 368 with a maximum variation of about 1%. This appears to be $C_{26}H_{54}$ (*M*, 366).

Fraction E. Old determination 394. The mean of eight observations in benzene was 369, and of four in chloroform 366, the variation being about 1%. This agrees with the molecular weight of $C_{26}H_{54}$, in which case E is isomeric with D, although the photographs are quite different.

Fraction F. Old value 419. The mean of eight observations in benzene was 390, and of nine in chloroform 396. Probably the substance is $C_{28}H_{58}$ (*M*, 394).

Fraction G. Old value 449 corresponding to $C_{32}H_{66}$. The photographs of G and of dotriacontane, reproduced in Fig. 1, are quite different. Three measurements in benzene with the new apparatus gave *M* 407. Three more by another investigator gave the same mean value. Three in chloroform gave 408, by the other observer 410. This hydrocarbon appears to be $C_{29}H_{60}$ (*M*, 408).

Fraction H. Previous value 434. Five determinations of *M* in benzene now gave a mean value of 443, and it is considered probable that this hydrocarbon is $C_{31}H_{64}$ (*M*, 436). It certainly is not dotriacontane (see Fig. 1).

These new magnitudes are shown in Table I, column 5.

TABLE I.

Substance.	Spacing in Å. units.	*n*, the number of carbon atoms in the molecule. Authors.	Beckmann.	Menzies and Wright.
Synthetic $C_{30}H_{62}$	40·4			
„ $C_{32}H_{66}$	42·7			
„ $C_{34}H_{70}$	45·3			
B	30·6	22	23	23
C	32·86	24	24	24
D	34·3	25	25	26
E	35·6	26	28	26
F	37·75	28	30	28
G	39·45	29	32	29
H (melted)	42·2	31·5	31	31
H (pressed)	42·9	31	31	31
Synthetic $C_{31}H_{64}$ (melted)	41·6			
„ $C_{31}H_{64}$ (pressed)	43*			

* Müller and Saville, this vol., p. 600.

In the case of hydrocarbons C, E, F, and G the number of atoms deduced from Dr. Christie's observations agrees with our estimate, for D there is agreement with the Beckmann value, whilst B and H differ. We give reasons below for considering that our measure of the spacing of hydrocarbon H corresponds to a value of n of 31; and we believe that the hydrocarbon B is $C_{22}H_{46}$, or at any rate contains this substance. A difference of one carbon atom in the chains of two of these hydrocarbons will separate the third-order lines in the photographs by about 0·33 mm. (see Fig. 1, H and dotriacontane), and as it is possible to measure a good plate to 0·01 mm. it is almost impossible to confuse two different substances. As is mentioned below, an absolutely uniform method of mounting the specimens is necessary.

We consider that the photographs show that the hydrocarbons obtained from paraffin wax are identical in constitution with the synthetic normal hydrocarbons for the following reasons.

(1) If the chains differed in nature, the unknown hydrocarbon line would not coincide in slope with the line on which the synthetic hydrocarbons lie.

(2) The intensity of the lines falls off uniformly with increasing order. There cannot be, therefore, a side chain attached to the main chain (Shearer, this vol., p. 597). If the end groups differed, then one line would lie above the other, the larger end groups being on the upper line. As the spacing measurement gives the minimum number of carbon atoms in the substance, the general agreement between this number obtained from the photographs and that deduced from the molecular-weight determinations makes it certain

that there are no more carbon atoms in the substances than are accounted for in the chains.

Whilst these experiments were in progress Müller and Saville completed a series of measurements of the spacings of the normal paraffin hydrocarbons, and found that the lower members had two modifications, A and B (this vol., p. 600). A comparison between our values and theirs shows differences much greater than the possible experimental error. This discrepancy is due to a difference in technique; Müller and Saville pressed crystal flakes on a glass plate, whilst we melted our specimens on the glass. Our measurements do not correspond to either the A or B modifications, from which we conclude that the lattice has been distorted by the melting on glass. We have been able to verify this by a measurement of hentriacontane, most kindly given to us by Dr. Müller. This substance when melted gives a spacing that falls on the line given by our other synthetic hydrocarbons; it is plotted in Fig. 2. The spacing we found for the same substance when its crystals were pressed on glass was much higher. An investigation into this behaviour is nearly completed and will be discussed in a separate communication. It is sufficient to state here that uniform treatment of the substances under investigation gives consistent results. Hydrocarbon H, when its crystals are pressed on glass, gives a spacing which agrees with that obtained by Müller and Saville (*loc. cit.*) for hentriacontane (see Table I). This substance is therefore hentriacontane. It remains to account for the anomalous value given by the melted substance.

Mixed Substances, melted together.—A photograph of crude paraffin wax is shown in Fig. 1 above that of fraction F. The lines of the two substances coincide—a remarkable fact, since fraction F only furnishes about 16% of the mixture; in fact it is not the most plentiful constituent. Measurement of the lines shows a very slight difference between the spacings, but as we have not been able to obtain more than three orders from the wax this difference may be partly experimental error. In general, however, we find that a mixture containing F shows only the F lines, slightly modified, provided the mixture is *melted* on the glass. Other mixtures, when melted together, usually yield modified lines of the longer chain, but if crystals of the two substances are pressed on the mounting the lines of both photograph unaltered. We consider that the anomalous spacing given by the melted specimen of hydrocarbon H may be ascribed to the presence of some impurity, too small in amount to show its lines in the photograph of the pressed substance. It will be noticed that the redetermination of the molecular weight of this substance does not give very satisfactory results; a similar

explanation will account for this. We believe the other hydrocarbons supplied by Prof. Francis to be fairly pure; the lines obtained fall very exactly on the normal hydrocarbon curve. Certainly those preceding and following F are not contaminated by this hydrocarbon to any appreciable extent. In the present state of our knowledge of the behaviour of mixed substances when examined by this method it is dangerous to generalise, but we believe that a normal spacing is at least an indication of a pure substance.

These experiments were carried out with the aid of a grant from the University Colston Research Society.

THE UNIVERSITY, BRISTOL. [*Received, July 15th,* 1925.]

CCXCVIII.—*Constituents of* Myoporum laetum, *Forst (the "Ngaio"). Part I.*

By FREDERICK HENRY McDOWALL.

THE first section of this paper deals with the aqueous extracts of various parts of the "ngaio" tree. Mannitol is present in the leaves to the extent of 0·2% (calculated on the weight of green leaves used), in the berries, which contain formic acid also, and in the wood to the extent of 0·25%.

The second section deals with the essential oil, 86% of which consists of an oxygenated sesquiterpene ketone, $C_{15}H_{22}O_3$, for which the author proposes the name "*ngaione*" (pronounced "ny-one") after the Maori name for the tree. Ngaione is characterised by its crystalline p-*nitrophenylhydrazone* and by its *semicarbazone*. The substance contains only one carbonyl group, and no methoxy- or methylenedioxy-group. It is reduced by sodium and alcohol to a secondary alcohol, *ngaiol*, which forms a monoacetate and a monomethyl ether. It is concluded that alcoholic hydroxyl groups are absent and that the molecule contains two separate oxide rings, since the presence of an organic peroxide ring would probably render the substance unstable (compare ascaridole, *loc. cit.*). The molecular refraction indicates that ngaione contains two ethylenic linkings. Since these remain unattacked by sodium and alcohol, they cannot be in the αβ-position to the carbonyl group, or conjugated with each other. Ngaione is thus probably an open-chain diolefinic ketone.

A solid paraffin hydrocarbon, $C_{32}H_{66}$ or $C_{34}H_{70}$, is also present in the essential oil.

Maiden (J., 1899, **55**, 665) isolated a resin from the exudations of *Myoporum platycarpum*, R. Br. No similar exudations occur on

Myoporum laetum, Forst. None of the species of *Myoporum* has been examined for essential oil.

Only a few substances of a like nature to ngaione have been isolated from essential oils. Apart from the well-known cineole, these are: Ascaridole, $C_{10}H_{16}O_2$ (Nelson, *J. Amer. Chem. Soc.*, 1911, **33**, 1404; Wallach, *Annalen*, 1912, **392**, 59); kessyl alcohol, $C_{14}H_{24}O_2$ (Bertram and Gildemeister, *Arch. Pharm.*, 1890, **228**, 483); calameone, $C_{15}H_{26}O_2$ (Soden and Rojahn, *Chem. Zentr.*, 1901, I, 1893; Thoms and Beckstrom, *Ber.*, 1901, **34**, 1021; 1902, **35**, 3187); kaempferia ketone, $C_{24}H_{28}O_4$ (Goulding and Roberts, J., 1915, **107**, 314); daucol, $C_{15}H_{26}O_2$ (Richter, *Arch. Pharm.*, 1908, **247**, 391); and dicitronelloxide, $C_{20}H_{34}O$ (Spornitz, *Ber.*, 1904, **47**, 478). Carlina oxide, $C_{13}H_{10}O$ (Semmler and Ascher, *Ber.*, 1909, **42**, 2355), is an aromatic compound, and elsholtzione, $C_{10}H_{14}O_2$ (Asahina and Murayama, *Arch. Pharm.*, 1914, **252**, 435; Asano, *J. Pharm. Soc. Japan*, 1919, **454**, 999), a furan derivative. Of the terpenic substances, the only one to which a constitution has been assigned is ascaridole (Wallach, *loc. cit.*). Many of these compounds, like ngaione, have a relatively high density.

Experimental.

Non-volatile Aqueous Extract.

(a) *Extraction of Leaves.*—The green leaves, after the essential oil had been removed by steam distillation, were extracted with water, and the filtrate was evaporated in a vacuum at 60°. The green residue gave to chloroform, ether, benzene, and light petroleum only a small quantity of colouring matter, but a hot alcoholic extract deposited, on cooling, white needles of mannitol, $[\alpha]_D$ (5% solution in presence of borax) +20·7°. After four crystallisations, this, alone or mixed with a genuine specimen, melted at 164—165°. On acetylation, it gave hexa-acetyl mannitol, m. p. 120°. The yield of mannitol was 10 g. from 5 kilo. of green leaves.

(b) *Extraction of Berries.*—The aqueous extract of the crushed berries was freed from tannin with lead acetate, boiled with animal charcoal, and evaporated in a vacuum. The residue yielded mannitol on extraction with hot alcohol.

(c) *Extraction of Wood.*—The residue from the aqueous extract of 1 kilo. of undried sawdust gave, when treated with alcohol, 2·5 g. of crude mannitol.

The Essential Oil.

The leaves and terminal branchlets (80 kilo. at a time) were distilled with superheated steam, 120 litres of distillate generally proving sufficient for complete extraction. The aqueous layer was

siphoned from the underlying layer of oil, and was then extracted twice with light petroleum. The yields ranged from 0·12% to 0·30%, varying with season and sample. The oil was cooled to −20° and the solid that separated (yield 0·01% of the crude oil) was recrystallised six times from hot absolute alcohol; m. p. 62—63° (Found: C, 85·4; H, 14·9; *M*, cryoscopic and ebullioscopic in benzene, 470. $C_{32}H_{66}$ requires C, 85·2; H, 14·8%; *M*, 450. $C_{34}H_{70}$ requires C, 85·3; H, 14·7%; *M*, 479). The substance is therefore a paraffin hydrocarbon of probable formula $C_{32}H_{66}$ or $C_{34}H_{70}$. The literature records the isolation of several similar compounds from essential oils (compare especially rose oil, *Bull. Soc. chim.*, 1904, **31**, 934).

The crystals were easily soluble in benzene, ether, chloroform, etc., slightly soluble in hot alcohol, but practically insoluble in cold alcohol. They were unaffected by bromine water or bromine in ether and were stable towards permanganate.

The clear oil, after removal of stearoptene, was of a reddish-brown colour and had a sweet malt-like odour; $d_{20^\circ}^{20^\circ}$ 1·0203; $[\alpha]_D$ −26·54°, $n_D^{20^\circ}$ 1·4823, saponification value, by direct titration after 2 hours' heating with alcoholic potash, 17·9. It was soluble in half its volume of 90% alcohol and in 4½ volumes of 70% alcohol. No seasonal variation was observed in the values of the constants. No nitrogen- or sulphur-containing substances were present (Found for crude oil: C, 71·5; H, 9·5%). The high density and high oxygen content seemed to indicate the presence of phenolic compounds, but treatment with caustic soda gave a yield of only 0·41% of phenols, and a methoxyl determination showed the absence of methylated phenols. From the low saponification value it was evident that lactones or esters were not present to any appreciable extent. The oil yielded no trace of aldehyde or ketone sodium bisulphite compound.

Repeated distillation of 850 g. gave the following fractions: up to 200°, 2 g.; 200—268° (in seven fractions), 22 g.; 160—166°/27 mm., 6 g.; 166—176°/27 mm., 8 g.; 176—182°/27 mm., 8 g.; 182—183°/27 mm., 730 g.; 183—189°/27 mm., 20 g.; non-volatile residue, 30 g.; loss, 24 g.

Ngaione.—The main fraction, b. p. 182—183°/27 mm., constituting 86% of the oil, is the only one so far examined. It was divided into three portions by repeated distillation, the refractive index of the last drop of liquid issuing from the condenser being used as a means of division in the absence of a boiling-point range. The middle portion (600 g.) was a lemon-yellow oil with a faint odour, $d_{20^\circ}^{20^\circ}$ 1·0276, $[\alpha]_D$ −26·20°, $n_D^{20^\circ}$ 1·4804. The substance is profoundly altered by distillation at ordinary pressures; b. p. 300°,

n_D, of distillate, 1·4900. Duplicate analyses indicated very consistently the formula $C_{16}H_{24}O_3$ (see, however, analyses of crystalline derivatives and of purified ketone, which agree closely with $C_{15}H_{22}O_3$) (Found for three separate samples: C, 72·6, 72·3, 72·6; H, 9·3, 9·3, 9·0; *M*, cryoscopic in benzene and ethylene bromide, 250. $C_{16}H_{24}O_3$ requires C, 72·7; H, 9·2%; *M*, 264. $C_{15}H_{22}O_3$ requires C, 71·9; H, 8·9%; *M*, 250).

The p-*nitrophenylhydrazone* was prepared by heating a filtered solution of 1 g. of *p*-nitrophenylhydrazine in 7 g. of alcohol and 7 g. of glacial acetic acid with 1·8 g. of the substance for 1 hour on the water-bath. After 24 hours, the emulsion produced on addition of water was extracted with ether. The extract was washed with dilute sulphuric acid and with sodium carbonate solution, dried, and the solvent evaporated over sulphuric acid. The residue of large, bright yellow tablets was washed with cold alcohol and recrystallised from warm alcohol; m. p. 103° (Found: C, 65·5, 65·4; H, 7·4, 7·1. $C_{21}H_{27}O_4N_3$ requires C, 65·4; H, 7·1. $C_{22}H_{29}O_4N_3$ requires C, 66·1; H, 7·3%).

The ketone (6 g.) and thiosemicarbazide (2·2 g.) were heated together in 30 c.c. of 63% alcohol on the water-bath for 12 hours; the alcohol was then evaporated, and the residue extracted with ether. From the extract a thick, reddish-brown oil, which could not be crystallised, was obtained (Found: S, 6·6. *Ngaione thiosemicarbazone*, $C_{16}H_{25}O_2N_3S$, requires S, 9·9%). The substance was treated in alcoholic solution with silver nitrate (2 equivs. were necessary for complete precipitation), and the yellow *silver* salt was filtered, washed with alcohol and ether, and dried (Found: Ag, 32·7. $C_{16}H_{24}O_2N_3SAg$ requires Ag, 25·0%. The double salt with silver nitrate requires Ag, 35·9%). The solid was therefore probably an impure double salt. Ngaione thiosemicarbazone was recovered from the silver salt as a thick syrup which could not be crystallised.

The silver compound (6·5 g.) was steam-distilled with excess of phthalic anhydride; the oil extracted from the distillate with light petroleum (yield 1·8 g.) had b. p. 185°/29 mm. (188° corr.), $d_{20^\circ}^{20^\circ}$ 1·0273, $^{*}n_D^{20^\circ}$ 1·4794, $[R_L]_D$ 69·10. $C_{15}H_{22}O_3$, requires $[R_L]_D$ 69·43 (Found: C, 71·9; H, 8·9. $C_{15}H_{22}O_3$ requires C, 71·9; H, 8·9%). This analysis and that of the *p*-nitrophenylhydrazone definitely establish the formula of ngaione as $C_{15}H_{22}O_3$.

Ngaione slowly reduced ammoniacal silver nitrate and Fehling's solution, more rapidly in presence of alcohol. It did not affect Schiff's reagent. In alcoholic solution it gave a bright green fluorescence with *m*-phenylenediamine hydrochloride, the colour being much more pronounced than that due to alcohol alone. It

did not, however, give a solid bisulphite compound under all conditions tried (compare kaempferia ketone, *loc. cit.*).

In an oximation experiment 63% of ngaione was converted in ½ hour and 76% in 2½ hours (Bennet, *Analyst*, 1909, 14). An alcoholic solution of ngaione (1 mol.) was heated with hydroxylamine hydrochloride (1¼ mols.) and sodium hydroxide (1⅝ mols.) on the water-bath for 5 hours. After removal of alcohol in a vacuum water was added, and the heavy oil extracted with ether. By distillation under reduced pressure the *oxime* was isolated as a lemon-yellow, viscous oil which could not be crystallised; b. p. 201°/27 mm., $d_{20°}^{20°}$ 1·0640, $[\alpha]_D$ (in 10% solution in chloroform) −13·51°, $n_D^{23°}$ 1·5008, $[R_L]_D$ 73·37. *Ngaione oxime*, $C_{15}H_{23}O_3N$, requires $[R_L]_D$ 73·74 (Found: C, 67·6; H, 8·6; N, 5·5. $C_{15}H_{23}O_3N$ requires C, 67·9; H, 8·7; N, 5·3%). The carbanilide of the oxime is a syrup.

The *semicarbazone* was prepared in aqueous alcoholic solution. After the mixture had been allowed to stand for a fortnight, water was added, and the precipitated solid dried on porous tile. No suitable crystallising medium could be found, the substance being extremely soluble in all solvents. Purified by reprecipitation several times from alcohol by the addition of water, it melted at 120—122° (decomp.) (Found: C, 62·9; H, 8·5. $C_{16}H_{25}O_3N$ requires C, 62·5; H, 8·2%).

The phenylhydrazone and *p*-bromophenylhydrazone are liquid. The substance would not form a semioxamazone even in the un diluted state at 170°; and under the conditions laid down by Doebner (*Ber.*, 1894, **27**, 852) as applicable to all aldehydes, it failed to yield a β-naphthacinchoninic acid. It also did not combine with freshly distilled pyruvic acid in presence of caustic soda (Lubrzynska and MacLean, *Chem. Zentr.*, 1914, 561), neither did it give a cyanoacetic acid compound. The failure to react with these aldehyde reagents, the slow nature of its combination with hydroxylamine, thiosemicarbazide, etc., the inertness towards sodium bisulphite and semioxamazide, all lead to the conclusion that the substance is a ketone. This conclusion is supported by the fact that an acid of the same number of carbon atoms cannot be obtained either by the use of oxidising agents or through dehydration of the oxime and subsequent hydrolysis. The reducing action toward Fehling's solution and silver nitrate is very sluggish, and, moreover, it does not appear to be due to the presence of the carbonyl group alone, since the purified alcohol (see below) also is slowly oxidised.

With boiling acetic anhydride ngaione is partially converted into the enolic acetate (saponification value 73. $C_{15}H_{21}O_2{\cdot}O{\cdot}CO{\cdot}CH$

requires 192). Ngaione decolorised bromine water very slowly; bromine in ether was rapidly absorbed, but the product was tarry.

Ngaiol.—With sodium (8 times the theoretical quantity) and absolute alcohol, ngaione formed an alcohol, *ngaiol* (yield 86%), which was purified through the acid phthalate, the usual proportions of benzene and phthalic anhydride being heated with the oil on a water-bath for 120 hours. The slowness of the reaction indicates the presence of a secondary alcohol, confirming the conclusion that the original substance is a ketone (combination takes place more rapidly without solvent at 130—140°, but is accompanied by a certain amount of racemisation). Ngaiol was thus obtained as a lemon-yellow oil with a faint sweet odour, b. p. 191—192°/29 mm. (195—196° corr.), $d_{20^\circ}^{20^\circ}$ 1·0163, $[\alpha]_D$ −25·00°, $n_D^{20^\circ}$ 1·4784, $[R_L]_D$ 70·28. $C_{15}H_{24}O_3$, $\equiv_2$, requires 70·94 (Found: C, 71·3; H, 9·8; M, cryoscopic in benzene, 260. $C_{15}H_{24}O_3$ requires C, 71·4; H, 9·6%; *M*, 252). These figures further check the formula suggested for the ketone. No trace of a pinacol was observed.

Treatment with the calculated quantity of chromic oxide in glacial acetic acid, instead of regenerating the ketone, completely disrupts a small proportion of the ngaiol, leaving the remainder intact.

All attempts to obtain a crystalline derivative of ngaiol have been unsuccessful (compare farnesol, which gives no crystalline derivatives). The acid phthalate and its *p*-nitrobenzyl ester (Reid, *J. Amer. Chem. Soc.*, 1917, **34**, 1249) are viscous syrups, and the phenyl- and α-naphthyl-urethanes are non-crystalline. The *methyl xanthate* (Tschugaev, *Ber.*, 1899, **32**, 213, 3332, etc.), purified from volatile products by steam distillation, is a mobile, light-yellow liquid (Found: S, 19·2. $C_{17}H_{26}O_3S_2$ requires S, 18·7%).

Ngaiol acetate, which is easily prepared in the usual way with acetic anhydride and sodium acetate, is a yellow oil, b. p. 190—192°/29 mm., $d_{20^\circ}^{20^\circ}$ 1·0337, $n_D^{20^\circ}$ 1·4720, $[R_L]_D$ 79·60. $C_{15}H_{23}O_2{\cdot}O{\cdot}CO{\cdot}CH_3$, $\equiv_2$, requires 80·31. Saponification value, 192. Theory for monoacetate, 185. The acetate decomposes slightly on distillation and for this reason always contains a small amount of free acetic acid. Heating with acetic anhydride in a sealed tube at 170—180° for 8 hours caused much resinification, but a small amount of oil was isolated, the saponification value of which was 204. Analysis showed that no water had been removed. By saponification with alcoholic potash and distillation in steam, ngaiol can be recovered from the acetate with unchanged physical constants.

The remaining two oxygen atoms are not attacked by acetic anhydride in presence of a drop of sulphuric acid at 0°. In order

as far as possible to avoid any hydrolysis of a sensitive ester group the product was isolated by distillation, after removal of sulphuric acid with calcium carbonate and decomposition of the excess of acetic anhydride by digestion with absolute alcohol. The saponification value of the product was 186.

Ngaiol benzoate cannot be prepared by the Schotten–Baumann method. By the pyridine method it is obtained as an oil which decomposes on distillation (compare daucol, *loc. cit.*). A quantitative experiment with benzoic anhydride according to Gascard (*J. Pharm. Chim.*, 1906, **24**, 97) showed that only one hydroxyl group was esterified. Ngaiol does not form a *p*-nitrobenzoate either by the Schotten–Baumann or the pyridine method.

Ngaiol monomethyl ether is a light yellow, almost inodorous oil. Three grams of potassium (2 mols.) were dissolved in 8 g. of pure tertiary amyl alcohol and 50 c.c. of dry toluene, and 10 g. of ngaiol were added to the hot solution. The mixture was cooled in running water while being gradually treated during 2 hours with excess (12 g.) of methyl iodide. After 12 hours, the mixture was warmed on the water-bath till neutral ($\frac{1}{2}$ hour), treated with water, and the toluene layer dried and distilled: b. p. 178—179°/29 mm. (182° corr.), $d_{20°}^{20°}$ 0·9913, $[\alpha]_D$ −16·82°, $n_D^{20°}$ 1·4701, $[R_L]_D$ 74·89. Calculated for $\frac{=}{2}$, 75·68 (Found: OMe, 11·1. $C_{15}H_{23}O_2{\cdot}OMe$ requires OMe, 11·6%). In the Zeisel determination ngaiol is converted into a resinous substance which dissolves completely in organic solvents. No deposit of carbon was formed, showing that a methylenedioxy-group is not present in the molecule.

Ngaiol methyl ether (3·30 g.) in dry boiling toluene dissolved one atom. of potassium in 6 hours and a second atom. in another 20 hours. The solution of potassium salt reacted slowly with methyl iodide in the cold. After 12 hours, the mixture was heated on the water-bath till neutral, and worked up in the usual way (Found for distilled product: OMe, 11·8%). It is noteworthy that calameone (*loc. cit.*) is regenerated unchanged when methyl iodide is allowed to act on its sodium salt.

The above experiments show that ngaiol contains probably only one hydroxyl group, and therefore that ngaione and ngaiol contain two internal ether groupings.

The work is being continued.

Part of this research was carried out at Otago University, Dunedin, New Zealand, while the author was holder of the John Edmond Research Fellowship. The still used in the extraction of the oil was obtained by aid of a grant from the New Zealand Institute. The author desires to express his thanks to the New Zealand

Institute and to the Chemical Society for research grants, and to Professor Inglis, Professor Collie, and Dr. Brady for their interest in the work.

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UNIVERSITY COLLEGE, LONDON. [*Received, June 11th*, 1925.]

CCXCIX.—*An X-Ray Examination of Maleic and Fumaric Acids.*

By KATHLEEN YARDLEY.

THE following investigation was undertaken primarily to determine whether the planosymmetry and centrosymmetry usually ascribed to maleic and fumaric acids respectively have any actual existence in the crystalline state. Maleic acid crystallises in the monoclinic system, and fumaric acid (as will be shown later) in the triclinic.

The crystallographic data for maleic acid ($M = 116$) are given by Groth ("Chemische Krystallographie," Part III, p. 286) as follows: Density $\rho = 1{\cdot}590$ g./c.c.; m. p. 130°; monoclinic prismatic, $a : b : c = 0{\cdot}7386 : 1 : 0{\cdot}7015$, $\beta = 117°7'$.

A preliminary investigation showed that the full (010) spacing was 10·11 Å.U. and substitution in the usual formula, $abc \sin\beta \,.\, \rho = 1{\cdot}65\, nM$, gives $n = 3{\cdot}96$ (4 mols./unit cell).

The spacings calculated on the basis $n = 4$ compare with the observed values as follows:

Plane (*hkl*).	Spacings calc.	Spacings obs.	Relative intensity of reflection.	Plane (*hkl*).	Spacings calc.	Spacings obs.	Relative intensity of reflection.
*100	6·67	3·31	Large.	310	2·17	2·16	Very small.
*010	10·14	$5{\cdot}05_5$	Very large.	210	3·18	3·17	Small.
*001	6·33	3·16	Very large indeed.	320	2·03	2·03	Moderate.
041	2·35	2·35	Mod. large.	110	5·57	5·56	Large IInd order only.
021	3·96	3·92	Moderate.	230	2·37	2·36	Very large.
023	1·95	1·92	Very small.	120	4·04	4·04	Mod. small.
301	1·85	1·85	Mod. small.	130	3·02	3·01	Mod. large.
30$\bar{1}$	2·51	2·48	Mod. large.	140	2·37	2·35	Small.
*20$\bar{1}$	3·74	1·85	Moderate.	160	1·63	1·63	Small.
*30$\bar{2}$	2·41	1·19	Very small.	180	1·24	1·25	Small.
101	3·81	3·76	Moderate IInd order only.	11$\bar{3}$	2·28	2·27	Small.
				111	3·57	3·57	Moderate.
10$\bar{1}$	6·22	6·22	Mod. large IInd order only.	11$\bar{1}$	5·30	5·30	Mod. large.
				22$\bar{1}$	2·96	3·02	Small.
*10$\bar{2}$	3·56	1·77	Small.	12$\bar{1}$	3·93	3·93	Mod. large.
410	1·64	1·64	Small.	13$\bar{1}$	2·97	2·95	Small.

The crystals show a perfect cleavage parallel to the (001) plane, and twin on (100) so frequently that a single crystal could not at first be obtained and the spectrometer measurements were made

on a twin. This gave rather complicated results, but it was generally possible to detect which additional reflections were the result of the twinning. For example, since the crystal is monoclinic and twins on (100), the $\{hkO\}$ zone is entirely unaffected and the reflections found are perfectly normal. The $\{h0l\}$ zone, however, shows doubling of its planes throughout. Fig. 1 represents the lattice of the twin (showing four unit cells) projected on the (010) plane.

The reflections from the (101), (001), (10$\bar{2}$), (10$\bar{1}$), (20$\bar{1}$), etc., planes of one individual (A) of the twin are apparently doubled owing to reflections from planes (20$\bar{1}$), (10$\bar{1}$), (10$\bar{2}$), (001), (101), etc., belonging to the other individual (B). The (100) plane shows, of course, a single reflection, since it is common to both individuals; the angular separation is greatest between the (10$\bar{2}$)A plane and the (10$\bar{2}$)B plane. Measurement of the angle (001)A : (001)B gave for the monoclinic angle, $\beta = 117°10'$.

Fig. 1.

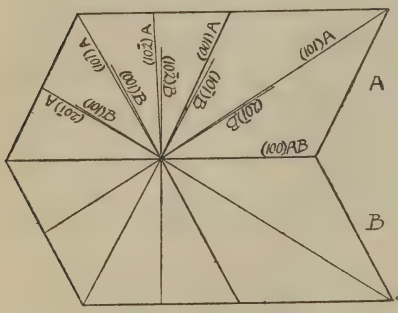
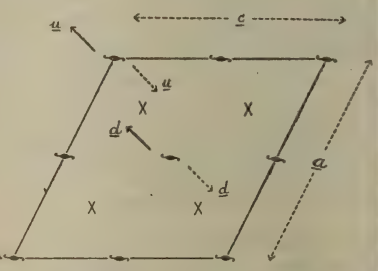


Fig. 2.



The reflections from planes of the $\{Okl\}$A zone may be confused with those from planes of the $\{hk\bar{h}\}$B zone, since the two zone axes are nearly parallel, and if one is vertical the other will be approximately vertical also. To eliminate all possibility of confusion of this kind, the measurements were repeated on a single crystal, grown from acetone after many attempts; several other planes also were measured. It was found, moreover, that, besides the perfect cleavage parallel to (001), there was an imperfect cleavage parallel to (010), and also that the crystals could be bent and twisted in certain directions without fracture. This interesting fact was verified both on single and on twinned crystals and will be described more fully in a separate paper.

The table of results shows that certain planes (marked *) have an observed spacing of only one-half of the calculated value. In other words, all odd-order reflections were absent from these planes. Apart from the (010) plane, all the marked planes have indices

$\{hOl\}$, where $(h + l)$ is odd. Since full spacings were found for the (301) (30$\bar{1}$) planes, the (101) (10$\bar{1}$) cannot really be halved, although only second-order reflections were found from these planes. The second-order reflection from the (010) plane was very strong, and moreover the planes for which k is odd gave much weaker reflections than those for which k is even. Thus the reflections from (011) and (031) could not be found, but those from (021) and (041) were quite strong; also the (160) and (180) reflections were easily measurable, whereas the (150) and (170) were not. The crystals therefore belong to the space-group C_{2h}^5, for which the (010) plane is halved and also all planes $\{hOl\}$ for which $(h + l)$ is odd (Astbury and Yardley, *Phil. Trans.*, 1924, *A*, **224**, 221). Rotation photographs, kindly taken by Dr. Müller, verified the spectrometer readings and the above conclusions. A diagrammatic representation of the space-group is shown in Fig. 2, in which the unit cell is projected on the glide-plane of symmetry, (010), and the positions of the centres of symmetry are marked by crosses.

Since there are four molecules in the unit cell, the maleic acid molecule must be asymmetric. The planosymmetry usually ascribed to maleic acid from chemical considerations has therefore no existence in the crystalline state. (It is, of course, possible that in solution the molecules do possess a plane of symmetry which is destroyed by slight distortion in the process of crystallisation). The absence of a plane of symmetry is perhaps surprising, as maleic acid on oxidation forms the internally compensated *meso*tartaric acid. It is, however, significant that, although maleic and succinic anhydrides are supposed to be isomorphous, the acids themselves are certainly not. Succinic acid belongs to the space-group C_{2h}^2 with two molecules per unit cell, and the molecule does, presumably, possess a plane of symmetry (Yardley, *Proc. Roy. Soc.*, 1924, *A*, **105**, 451), but its crystals are quite unlike those of maleic acid except in that they belong to the same class. The co-ordinates of equivalent points of the four molecules of maleic acid in the unit cell, relative to the crystallographic axes, are (000), $(\frac{1}{2}v\frac{1}{2})$, $(u\frac{1}{2}w)$, $(u + \frac{1}{2}, v + \frac{1}{2}, w + \frac{1}{2})$. Exact consideration of the relative intensities of reflection from different planes is not likely to be very helpful in deciding the values of the variable parameters, u, v, w, as the positions of the atoms in the molecule are not known. There are, however, some general indications of their value. For instance, since very large second-order but no first-order reflections were found for the (101) (10$\bar{1}$) planes, it seems probable that u and w are approximately equal to $\frac{1}{2}$ and 0 or 0 and $\frac{1}{2}$. Also the exceptionally large reflection from the (001) planes, parallel to which is an excellent cleavage, indicates that most of the atoms lie in these planes and

very few between them. The following structure is suggested as being most probably near to the truth, though not by any means as being correct in every detail. In general, the actual measurements completely define the lattice and space-group, but the

FIG. 3.

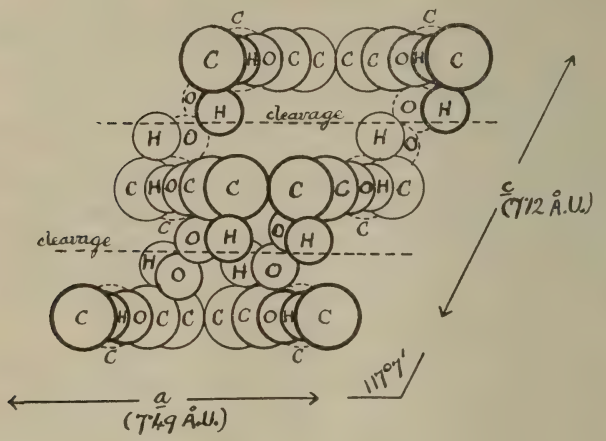
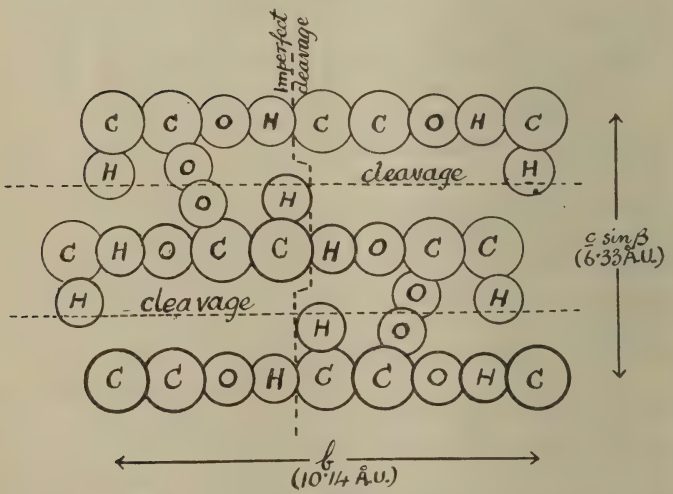


FIG. 4.

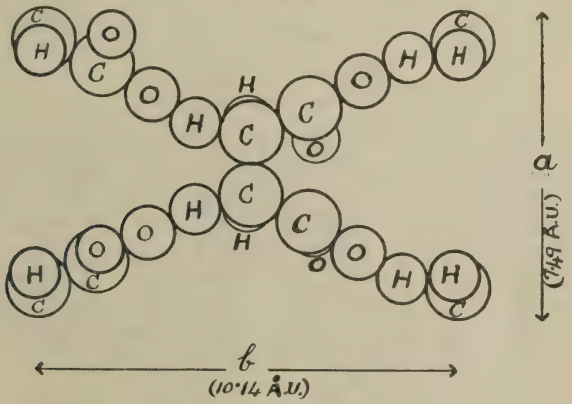


assignment of a structure, however probable or plausible, is alway accompanied by a certain amount of conjecture. The suggeste structure for maleic acid is based on the known space-group C_{2h}^5 an therefore on the simple Bravais lattice Γ_m. In order to explai the very large reflection from the cleavage plane (001) it is necessar

to assume that the double bond lies along the a axis and the two C–C–OH groups lie wholly in the (001) plane, linking between the (001) planes being effected by means of the ketonic oxygen atoms only. Since it is not probable that two ketonic oxygen atoms will attract each other with any great force (indeed, repulsion is more likely), the cleavage parallel to the (001) planes is readily explained. This is illustrated diagrammatically in Figs. 3 and 4.

In Fig. 3 is shown the projection of the unit cell on the (010) plane of symmetry. The measurements show that the molecule at the point $(\frac{1}{2}, v, \frac{1}{2})$ is the reflection of that at the origin. The only satisfactory way of placing the remaining two molecules is for the molecule which is obtained by rotation of that at the origin to lie at

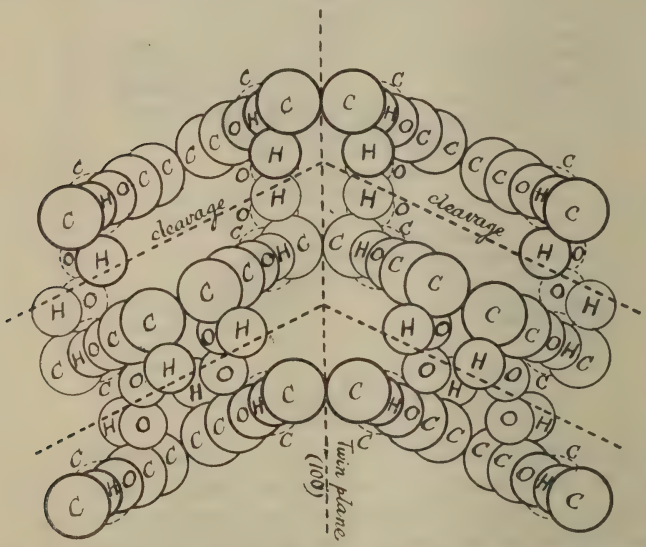
FIG. 5.



or very near the point $(\frac{1}{2}, \frac{1}{2}, 0)$ and for the molecule which is centrosymmetric with respect to that at the origin to lie at the point $(0, v + \frac{1}{2}, \frac{1}{2})$. The ketonic oxygen atoms lie approximately parallel to the c axis when projected on to the (010) plane. In Fig. 4, the projection is on a plane normal to the a axis. Here both cleavages are clearly seen, and it will also be noticed that the hydrogen of the carboxyl group of one molecule links on to the unsaturated carbon of the next. The exact positions of the hydrogen atoms cannot, of course, be fixed, since their scattering power is too small seriously to affect the X-ray reflections. In Fig. 5, which shows just the atoms lying in the (001) plane and those directly connected to them, the asymmetry of the molecule is at once apparent, and a comparison of the various diagrams shows that such asymmetry is necessary to build up the monoclinic structure. It is essential that such a structure should explain the almost invariable twinning on the (100) plane. Multiple twinning never appeared at all; in fact, examination of the crystals at various stages of their growth tended

to prove that a crystal began to grow at the twin plane and then built itself up to equal amounts on either side of this. The material crystallised at first in long, fine needles, which afterwards increased in thickness. However fine these needles might be, they were always perfect twins, and the smaller the crystal the more nearly exactly was it bisected parallel to its length by the twin plane. If these needles were broken across, a remarkably good re-entrant cleavage was observed, parallel to the (001) plane in each individual of the twin. In the case of a cluster of needle-like twins growing out from a complex nucleus, the apex of the re-entrant angle cleavage always pointed towards the nucleus, showing that the crystal growth

Fig. 6.

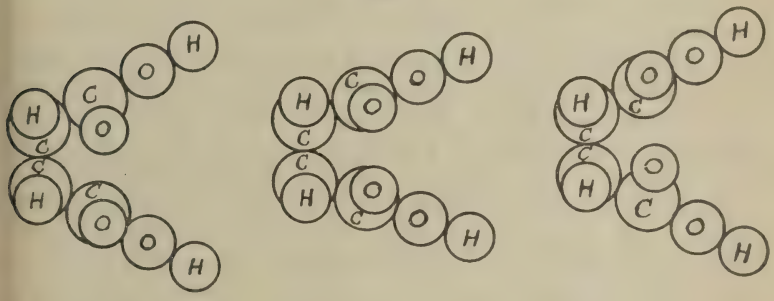


had followed certain clearly defined lines in the case of each needle. When crystallisation had taken place fairly rapidly, none of the crystals were single, although by slowing down the rate of evaporation it was sometimes possible to obtain large crystals which had grown unevenly on either side of the twin plane. From these one or two single individuals could be detached. Now if we assume that the crystals start growing as single individuals and then suddenly change direction and form twins, it is not easy to explain either the absence of multiple twinning or the presence of twinning in the very smallest crystals. These facts are readily explained on the hypothesis that growth begins at the twin plane. In that case, since the twin plane is a plane of reflection, molecules lying in it would necessarily possess a plane of symmetry, and would

therefore be slightly different from those in the main body of the crystal. This is not improbable, as a little consideration will show. The molecules in the suggested structure are distorted but very little out of their symmetrical form; in solution, these molecules probably do possess a plane of symmetry (or other two-fold symmetry), since there is no reason from a chemical point of view why one-half of the molecule should differ from the other. When, therefore, crystallisation first begins, it is probable that the molecules will form themselves into a sheet, retaining their original symmetry. On either side of this sheet the crystal would build itself up as shown in Fig. 6.

The molecules on either side of the central twin plane would be pulled out by the next succeeding layer and thus would become asymmetric, but the molecules lying *in* the twin plane, being pulled

FIG. 7.



equally on either side, would not lose their plane of symmetry. The re-entrant cleavage is also easily explained. It is to be expected that at the twin plane the structure would be somewhat strained; in fact, the two individuals can be separated at the twin plane, though there is no cleavage parallel to the (100) plane in any other part of the crystal. An asymmetric molecule and its reflection are non-superposable and so, unless it is assumed that the asymmetry is merely distortion produced during the process of crystallisation, it is impossible to avoid the conclusion that the original solution contained two enantiomorphous kinds of molecules. This is most unlikely.

In Fig. 7, (*b*) represents the undistorted molecule with its plane of symmetry, as it would occur at the twin plane; (*a*) and (*c*) show the molecule distorted in opposite directions, thus accounting for the asymmetric enantiomorphous forms. The approximate atomic diameters in this structure are: C = 1·54 Å.U., O: = 1·15, OH = 2·5, H = 1·15. It is not possible to tell whether the atomic diameter

of the unsaturated carbon atom differs from that of the saturated, especially as in the suggested structure both carbon atoms are, in effect, saturated.

The measurement of crystals of fumaric acid was much more difficult than that of maleic acid. No previous crystallographic data were available, as the crystals grown are utterly unsuited to the usual goniometric examination. They are small and copiously twinned in many directions, and most crystals show either no clear face at all or only one. Nearly all of the fumaric derivatives that have been measured belong to the triclinic system, and it seemed probable that that would prove to be the case for the acid also. Fortunately, by slow evaporation of an aqueous solution, one crystal was obtained that seemed to be twinned in one direction only. Measurements were made on this crystal, the Bragg ionisation spectrometer being used (as before) together with a Coolidge tube of rhodium anticathode. The main planes were first localised by obtaining the "mirror" reflection of "white" X-radiation, and the position of the actual reflection of the homogeneous X-ray beam could then be found quite easily. The crystal was almost shapeless, but it showed one bright, though by no means plane, face. By setting this face as nearly as possible vertical and then rotating the crystal about it very slowly, the main zone axes were found and planes in three principal zones were measured. The unit cell was triclinic. The face which actually grows on some crystals was taken as the (001). The crystal measured was twinned on this plane, which was also a good cleavage plane. Nearly at right angles to it was a second, less definite, cleavage plane which was taken as the (010). A third plane nearly normal to these two was taken as the (100). These planes having been arbitrarily selected as axial planes, the spacings of other planes in the axial zones were measured. By combining all the observations it was possible to determine the size of the minimum crystallographic cell. The unit cell taken is, of course, in the triclinic system, only one of an infinite number of minimum cells all having the same volume. The conditions that any such unit cell must fulfil are (1) that no calculated spacing should be a sub-multiple of the corresponding measured spacing, and (2) that no set of calculated spacings should be multiples of the measured spacings of those planes. If, for example, the measured spacing of each plane with indices $\{hkl\}$, where h is odd, were one-half of the calculated value, it would mean that the unit cell adopted was twice as large as the true unit cell, the a axis of the latter being only one-half the length of the a axis formerly used.

Considerations such as these showed that the arbitrarily selected axial planes did form the boundaries of one such possible minimum

cell. The angles between the axial planes and their spacings were measured; the lengths of the axes and the axial angles calculated therefrom are $a = 7{\cdot}56$, $b = 15{\cdot}00$, $c = 6{\cdot}20$ Å.U., whence $a : b : c = 0{\cdot}504 : 1 : 0{\cdot}413$ and $\alpha = 90°40'$, $\beta = 88°30'$, and $\gamma = 89°48'$.

As these angles are all very nearly right angles, they are almost exact supplements of the measured angles between the axial planes. Also the differences between the lengths of the axes a, b, c, and the observed spacings d_{100}, d_{010}, d_{001} are less than the probable errors of observation and are therefore negligible. From these axial spacings and angles the spacing, d, of any other plane (hkl) can be calculated by means of the formula

$$\frac{N^2}{d^2} = \frac{h^2}{a^2}\sin^2\alpha + \frac{k^2}{b^2}\sin^2\beta + \frac{l^2}{c^2}\sin^2\gamma + 2\left[\frac{kl}{bc}(\cos\beta\cos\gamma - \cos\alpha) + \frac{lh}{ca}(\cos\gamma\cos\alpha - \cos\beta) + \frac{hk}{ab}(\cos\alpha\cos\beta - \cos\gamma)\right]$$

$$= \sum\frac{h_2}{a_2}\sin^2\alpha + 2\sum\frac{kl}{bc}(\cos\beta\cos\gamma - \cos\alpha),$$

where $N^2 = 1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma$

$$= 4\sin\tfrac{1}{2}(\alpha+\beta+\gamma)\sin\tfrac{1}{2}(-\alpha+\beta+\gamma)\sin\tfrac{1}{2}(\alpha-\beta+\gamma)\sin\tfrac{1}{2}(\alpha+\beta-\gamma).$$

Also the angle θ between two planes $(h_1k_1l_1)$ and $(h_2k_2l_2)$ is given by

$$\cos\theta = \frac{d_1d_2}{N^4}\left[\frac{h_1h_2}{a^2}\sin^2\alpha + \frac{k_1k_2}{b^2}\sin^2\beta + \frac{l_1l_2}{c^2}\sin^2\gamma + \frac{h_1k_2 + h_2k_1}{ab}(\cos\alpha\cos\beta - \cos\gamma) + \frac{k_1l_2 + k_2l_1}{bc}(\cos\beta\cos\gamma - \cos\alpha) + \frac{l_1h_2 + l_2h_1}{ca}\cos\gamma\cos\alpha - \cos\beta)\right]$$

$$= \frac{d_1d_2}{N^4}\left[\sum\frac{h_1h_2}{a^2}\sin^2\alpha + \sum\frac{k_1l_2}{bc}(\cos\beta\cos\gamma - \cos\alpha)\right],$$

d_1, d_2 being the spacings of the two planes.

The volume of the unit cell is $abcN$.

Comparison can thus be made between the spacings and angles calculated as above and those actually measured on the spectrometer.

Spacings.

Plane.	Calc.	Obs.	Relative intensity.	Plane.	Calc.	Obs.	Relative intensity.
100	—	7·56	Small II.	$30\bar{1}$	2·36	2·36	Mod. large.
010	—	15·00	Moderate VI.	101	4·73	4·74	Very small I, small III.
001	—	6·20	Small I, very large II.	$10\bar{1}$	4·86	4·83	Very small I, small III.
012	3·04	3·04	Mod. large.				
$01\bar{2}$	3·03	$3{\cdot}03_5$	Mod. large.	110	6·74	6·70	Mod. small II, III.
031	3·91	$3{\cdot}89_5$	Moderate.	$1\bar{1}0$	6·76	6·75	Mod. small II, III.
$03\bar{1}$	3·87	$3{\cdot}88_5$	Moderate.	210	3·66	3·59	Moderate.
041	3·23	—	Not found.	$2\bar{1}0$	3·67	$3{\cdot}60_5$	Mod. large.
$04\bar{1}$	3·19	3·20	Small.	140	3·36	3·35	Small.
301	2·31	2·32	Mod. large.	$14\bar{0}$	3·37	3·37	Small.

Angles between planes.

Planes.	Calc.	Obs.	Planes.	Calc.	Obs.
010 : 001	—	89° 20′	$30\bar{1}$: 001	69° 10′	68° 51′
001 : 100	—	91 30	$10\bar{1}$: 001	141 17	141 20
100 : 010	—	90 12	$10\bar{1}$: 001	39 56	39 36
012 : 001	168° 24′	168 12	$1\bar{1}0$: 010	116 57	116 40
$01\bar{2}$: 001	11 35	11 37	$1\bar{1}0$: 010	63 25	63 17
$03\bar{1}$: 001	128 31	128 32	$2\bar{1}0$: 010	104 19	104 18
$03\bar{1}$: 001	50 42	50 43	$2\bar{1}0$: 010	76 3	76 8
041 : 001	58 21	58 32	$14\bar{0}$: 010	153 31	153 36
301 : 001	113 25	113 28	$14\bar{0}$: 010	26 34	26 50

Allowance being made for the obvious difficulties in setting the crystal on the spectrometer table in the correct position, this agreement is quite good.

The density of fumaric acid is 1·625 g./c.c. and $M = 116$. Calling the number of molecules per unit cell n, we have $abcN\rho = nM$. 1·65. Substitution of the known values of a, b, c and N leads to the value $n = 5{\cdot}97$.

This shows that there are six molecules of formula $C_2H_2(CO_2H)_2$ in the unit cell, the *minimum* cell which, repeated through space, will build up the crystal structure. It is well-known, however, that the number of asymmetric units required to build up a triclinic cell is either one or two. A triclinic pedial (C_1) crystal is formed by the repetition through space of a single asymmetric unit, a triclinic pinakoidal (C_i) crystal by the repetition through space of one centrosymmetric unit or of two asymmetric units arranged centrosymmetrically with respect to each other. Now it is impossible from the outward form of the fumaric acid crystals to tell whether they belong to the pedial or to the pinakoidal class, since all the crystals are practically shapeless, nor is it possible by any *X*-ray method to distinguish between the two classes. If the crystals belong to the pedial class, then it follows that six simple molecules of formula $C_2H_2(CO_2H)_2$ must, in the solid state, be associated together to form a single asymmetric unit, which is then repeated through space. If, on the other hand, the crystals are pinakoidal, then the six molecules in the unit cell are arranged in two groups of three, each group being asymmetric in itself, but centrosymmetric with respect to the other. It is important to know whether the simple chemical molecules in such a group are related to one another in a manner different from that in which they are related to all other molecules in the crystal. If this is so, then the group might be called a "crystal molecule," its formula being $[C_2H_2(CO_2H)_2]_6$ in the first case or $[C_2H_2(CO_2H)_2]_3$ in the second. In the unit cell of any symmetrical crystal there exists an association of a given number of ultimate asymmetric parts which are so arranged about the elements of symmetry as to build

up a unit possessing the full symmetry of the class. This unit then repeats itself through space without change of character or orientation. In general, the ultimate asymmetric parts are identical with the chemical molecule (or ions) or are sub-multiples of the chemical molecule. Thus, in the case of naphthalene the molecule is centrosymmetric (that is, it contains two such parts) and two molecules arranged about an axis of screw symmetry build up the unit monoclinic prismatic cell. There is certainly no reason why one should pair a given molecule in such a crystal with any of its four immediate neighbours and call such a pair a double molecule. The case of fumaric acid is, however, quite different. This is one of the few exceptional crystals where the ultimate asymmetric part is a multiple of the simple chemical molecule. Other examples which have been found include α-naphthylamine (Sir W. H. Bragg, Report of the Solway Conference, 1925), where the orthorhombic cell contains eight asymmetric groups of three chemical molecules; monoclinic carbon tetrabromide (Mark, *Ber.*, 1924, **57**, 1820), where the ultimate part is said to be C_2Br_8; and rhombic sulphur (Mark and Wigner, *Z. physikal. Chem.*, 1924, **111**, 398), in which the unit cell contains 128 atoms, the ultimate asymmetric group being either S_4, S_8, or S_{16}. As a rule, when two or more chemical molecules are associated together in the unit cell it is with the object of producing symmetry. When, as in these exceptional cases, there is also an association of a type which does not produce symmetry, we are perhaps justified in assuming that this association is closer than a mere crystallographic connexion and partakes more of the nature of an actual polymerisation in the solid state. In the case of sulphur it is most probable that the different crystalline forms are polymerised to different extents; the polymerisation is known to persist to a certain extent even in the vapour. This point has not been tested in the case of fumaric acid. Very little is known about matter in the solid state, apart from what can be directly deduced from the crystal structure. The fact that fumaric acid sublimes at 200° and melts in a closed tube only at 286—287° may perhaps be taken as evidence of a closer association between the chemical molecules than that usually existing in crystals. The same possibly applies to its insolubility in all ordinary solvents, and to its low heat of combustion (317·6 mol.-gm.-cals.) compared with that of maleic acid (331·3 mol.-gm.-cals.), since it may well be supposed that in the case of fumaric acid heat would be used up in separating the molecules before actual combustion could take place. It is doubtful, however, whether any reliance can at present be placed on conclusions drawn from differences in heats of combustion, heats of solution or crystallisation, etc., since we have very little idea to

what extent these depend on the actual crystal structure and to what extent on the molecular structure (Garner and Randall, J., 1924, **125**, 881). Bruni and Gorni (*Gazzetta*, 1900, **30**, i, 80), when determining the molecular weights of methyl maleate and fumarate cryoscopically in methyl succinate, found a normal value for the maleic ester (149·5 to 164; calc., 144), but the abnormal value of 797 to 914 for the fumaric ester in dilute solution; a raising of the freezing point of more concentrated solutions (above 2%) probably indicated the formation of a solid solution of the fumaric with the succinic ester. The abnormal value obtained for the fumaric ester in dilute solution may possibly be due to molecular association of the same type as that now observed in the case of the acid. Deductions drawn from the behaviour of the esters could not, however, be safely applied to the acids. That there is some difference between maleic and fumaric acids other than this association is obvious, since in solution they both act as if they had the simple formula and yet there are striking chemical differences to be accounted for. Probably there is a difference in the spatial arrangements of the atoms in the simple molecules in solution, but in neither case does the molecule possess symmetry in the crystalline state.

FIG. 8.



The complex twinning mentioned above as characteristic of fumaric acid is worth describing in some detail. Cruciform growths are very frequent (as shown in Fig. 8). The only distinct face on such a twin is the flat surface, from which a small reflection has been obtained showing it to be the {001} plane. The twin planes therefore have indices {*hkO*}. The angles between the arms of the twin are almost exact right angles and the *b* axis runs parallel to the length of the arms. Hence the twin planes must be the {120} and {1$\bar{2}$0}, which make angles of 44°42′ and 44°55′ respectively with the {010} plane. Some crystals are twinned in the above manner and then again each arm is twinned on a plane nearly at right angles to both {001} and {010}, presumably therefore the {100}. Such interpenetrating twins obey at least two twin laws. Other interpenetrating twins have not merely four arms, but six. Some have only four arms, but these are not at right angles. The laws obeyed by such twins have not yet been elucidated.

More recent *X*-ray examination of some of the derivatives of maleic and fumaric acids has shown that in no other case yet investigated does association take place in the solid state. The substances examined were monopotassium chloromaleate, $C_4H_2O_4ClK$,

diammonium chlorofumarate, $C_4HO_4Cl(NH_4)_2$, and ammonium hydrogen fumarate, $C_4H_3O_4NH_4$; the *X*-ray data obtained have been published elsewhere (Yardley, *Phil. Mag.*, 1925, **50**, 864).

In conclusion, I wish to thank Professor Sir William H. Bragg, F.R.S., most heartily for his constant encouragement and advice. My grateful acknowledgments are also due to the Advisory Council of the Department of Scientific and Industrial Research and to the Royal Institution for rendering financial and laboratory assistance. For the preparation of the three compounds last mentioned, I am very much indebted to Mr. W. B. Saville.

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CCC.—*Purification of Phosphoric Oxide.**

By HENRY WHITAKER.

FINCH and PETO purified phosphoric oxide from traces of lower oxides by subliming it in a current of oxygen in an iron tube, heated to redness, and collecting the sublimate in a cooled glass tube (J., 1922, **121**, 692). On repeating the experiment, the chief difficulties encountered were the blocking of the glass tube with a solid crust of oxide and its frequent fracture at the glass-to-iron junction. Better results were obtained by employing a special form of receiver.

The receiver shown in Fig. 1 consists of a T-piece of wide glass tubing, the lower end, *b*, of which is fitted by means of a cork to the wide-necked bottle, *c*; transference of the sublimate from the receiver to a bottle for storage is thus avoided.

The receiver shown in Fig. 2 was made by sealing the wide tube, *b*, close to the end of a (broken) Liebig's condenser jacket, which was drawn out at *e* to fit into the end of the iron tube. The glass ram, *a*, served to rake down into the bottle any deposit which collected at *f*, and the tube *b* was kept clear by occasional raking with a glass rod, applied through *d*, which was normally closed with a cork. In the glass-to-iron junctions at *e*, a packing consisting of a collar of thin asbestos paper was found preferable to cementing with phosphoric acid. The chief drawback of either form of receiver, however, was fracture, which invariably occurred sooner or later in the course of the experiment. An iron T-piece was next tried, which proved more satisfactory.

* The work now described was completed in 1922. The peculiar difficulties attending the distillation of phosphoric oxide are disclosed by the work of Smits and Rutgers (J., 1924, **125**, 2573).

The bent glass tube, with rake, employed by Finch and Peto for admitting small quantities of phosphoric oxide at a time into the iron tube was found to be inconvenient, and a simple form of feeding apparatus was substituted, which proved entirely successful. It consists of a wide glass tube, drawn out and sealed to the end of a thinner glass tube and provided with an ordinary cork, through which passes a glass rod flattened at the end into a circular disk. The glass rod should slide easily through the cork and the circular disk should loosely fit the narrow tube. The dropping tube is charged by raising the cork, keeping the glass rod in position with



Fig 1.

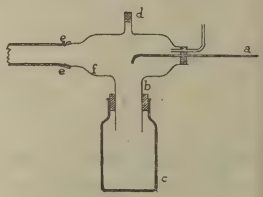


Fig 2.

Fig 3.

the disk closing the narrow tube; the cork is then slid back into position. The crude phosphoric oxide contained in the dropping tube can be admitted as required, by slightly raising the glass rod and tapping the tube. This form of apparatus can be repeatedly recharged with fresh phosphoric oxide without interrupting the experiment.

Blockages tended to occur in the vertical limb of the central iron T-piece; these were eliminated by using a vertical tube of wider diameter than the horizontal portion. The final form of the apparatus is shown in Fig. 3.

The current of oxygen (dried by passage through sulphuric acid, stick caustic potash, and crude phosphoric oxide) enters the iron

tube at *e*. It was found unnecessary to have an exit tube for the escaping oxygen. By properly adjusting the "fit" of the bottle *c* (receiver for the sublimed phosphoric oxide) to the cork *b*, fitted over the iron tube, *a*, the oxygen escaped *viâ b*. During the progress of an experiment, the plug, *d*, is unscrewed occasionally and the iron T-piece raked with an iron rake.

In one experiment, from approximately 200 g. of impure phosphoric oxide, 70 g. of pure pentoxide were obtained in 2 hours. This product, tested with silver nitrate in the manner suggested by Finch and Peto, was found to be free from lower oxides.

The use of mercuric chloride as a reagent for detecting the presence of lower oxides of phosphorus (suggested by Sir Richard Threlfall in a private communication to Professor A. Smithells) was found to be more convenient than silver nitrate, as neutralisation of the phosphoric acid with sodium hydroxide is unnecessary. A small quantity of the phosphoric oxide to be tested, dissolved in water, is boiled with mercuric chloride solution; if traces of phosphorous acid are present, a white turbidity or precipitate of mercurous chloride appears. All the samples of phosphoric oxide prepared by the method described above, when thus tested, were found to be free from lower oxides.

THE UNIVERSITY, LEEDS. [*Received, August 20th*, 1925.]

CCCI.—*Determination of Metals Dissolved in Mercury. Rapid Method of Purifying Mercury.*

By ALEXANDER SMITH RUSSELL and DEREK CURTIS EVANS.

THE work to be described is dependent on two observations, both of which, we think, are new: (1) that all metals more electropositive than mercury except cobalt go rapidly into solution as sulphates without the accompaniment of mercury when amalgams of them are shaken with potassium permanganate or certain other oxidising agents in dilute sulphuric acid, and (2) that the point at which the last trace of the metal in the mercury has gone into solution is shown by the breaking of the surface of the mercury into bubbles. For the determination of single metals in mercury by the method to be described it is necessary that the reducing power of the metal be 100%, that is to say, that the metal go into solution only in so far as it reduces the permanganate or other oxidising solution. For purifying mercury, on the other hand, rapidity of action between the metals to be removed and the

oxidising solution is more necessary than efficiency of reducing power.

We find * that the order in which metals when dissolved in mercury are removed from it by oxidising solutions is not the same as that of the electrode potentials of the metals in the free state. This order in mercury is (proceeding from electropositive to noble metals and including only those with which we have experimented) : zinc, manganese, cadmium, thallium, tin, lead, copper, chromium and iron, bismuth, cobalt, mercury, and nickel. It was found by obtaining the metals two at a time in mercury and finding out which went first into solution when ferric sulphate, or potassium permanganate or uranyl sulphate in sulphuric acid was reduced. The order seems quite definite; it appears to be the same whatever oxidising solution be reduced, whether the solution be hot or cold, whether sulphuric or hydrochloric acid be employed, and whatever other metals be present in the amalgam. The order in mercury differs from the order of the electrode potentials of metals in the free state only in the absolute positions of chromium, manganese, iron, cobalt, and nickel (atomic numbers 24 to 28). This is ascribed to passivity (Russell, *loc. cit.*). The relative order of these elements in both series is the same.

Experimental.

The reducing efficiency of a metal in mercury was investigated as follows : an amalgam containing from 0·2 to 0·4 g. of the metal in 200 g. of mercury was prepared either by direct solution, or by electrolysing solutions of sulphate in sulphuric acid the concentrations of which before and after electrolysis had been determined; the amalgam was shaken in a 300 c.c. stoppered bottle with 80 c.c. of $2N$-sulphuric acid and a volume of accurately $N/10$-potassium permanganate until the pink colour was just discharged; further volumes of permanganate were run into the bottle and the colour discharged until a point was reached such that on further shaking the surface of the mercury became a mass of small bubbles. This point could be accurately judged with experience to about 0·2 or 0·3 c.c. and was taken as the point at which the whole of the metal had left the mercury. The mass of the metal theoretically necessary to oxidise the volume of reduced permanganate was then compared with the known weight contained originally in the mercury.

* This experimental work with discussion will be published elsewhere In *Nature*, 1925, **115**, 455, one of us (A. S. R.) gave this order slightly differently. By a slip *chromium* read *manganese*. The position of manganese had not then been investigated.

The results obtained for seven metals and potassium permanganate are in the table below.

Gram taken.	Gram found.	% efficiency.	Gram taken.	Gram found.	% efficiency.
	Zinc.			Lead.	
0·210	0·193	91·9	0·100	0·101	101
0·210	0·192	91·4	0·202	0·200	99
0·219	0·200	91·3	0·205	0·206	100·5
0·929	0·865	93·1	0·206	0·206	100
			0·406	0·410	101
	Cadmium.			Copper.	
0·222	0·222	100	0·1115	0·1115	100
0·230	0·228	99·1	0·1673	0·1680	100·4
0·263	0·261	99·2		Iron.	
0·281	0·279	99·3	0·1791	0·1722	96·1
	Tin.		0·3658	0·3515	96·1
0·400	0·400	100		Bismuth.	
0·401	0·402	100·2	0·302	0·302	100
0·403	0·400	99·2	0·367	0·365	99·5
0·403	0·401	99·5			

It is seen that the results obtained by this rapid method (an experiment could be easily completed in 5 minutes) are fairly consistent and that each metal tried, with the exception of zinc and iron, is 100% efficient as oxidiser of potassium permanganate. These results contrast remarkably with the reducing efficiencies, and also the rate of oxidation, of some of these metals in the free state as investigated by Thorpe (J., 1882, **41**, 287) and Sugden (J., 1921, **119**, 233).

The results obtained in a similar manner when the metals reduced a $N/10$-solution of ferric sulphate in $2N$-sulphuric acid were approximately 100% for cadmium, tin, lead, copper, and bismuth, as with permanganate. Zinc, however, was now also 100% efficient, the actual values obtained being 100, 100·9, and 100·1. The reducing efficiency of iron was, however, again less than 100%, the values obtained varying from 94 to 97. Ferric sulphate was found to oxidise the metal of the amalgam much more rapidly than permanganate, and shaking had to be carefully done to avoid over-running the end-point and bringing some of the mercury itself into solution.

When uranyl sulphate was reduced, none of the metals showed reducing efficiencies of 100%. Of the seven metals mentioned above, only zinc, cadmium, tin, and lead could be investigated, because these alone were found to reduce uranium quantitatively from the sexavalent to the quadrivalent form. The mean values of their efficiencies decreased in decreasing order of potential, the mean values found being 91, 88, 82, and 74 for zinc, cadmium, tin, and lead, respectively.

It is obvious that the reducing efficiency of a metal may be investigated in this way only when it is completely removed from the mercury without being accompanied by mercury. It was found that mercury invariably accompanied cobalt and nickel when amalgams of these elements were shaken with oxidising solutions. The number of atoms of cobalt oxidised by the permanganate was found to be greater than that of mercury, and the number of atoms of nickel less. Cobalt appears, therefore, to act like a more electropositive and nickel like a more electronegative metal than mercury. It was found possible by sacrificing some mercury to remove the whole of the cobalt, but not the whole of the nickel from the mercury by shaking with oxidising solutions. These are the only metals which lie in potential between zinc and mercury in the free state which cannot be determined quantitatively by the method described in this paper.

The whole of these results receive a ready explanation with the help of present knowledge of the phenomenon of over-voltage. When a metal dissolved in, and more reactive than, mercury is shaken with sulphuric acid, it goes to some extent into solution and the equivalent amount of ionic hydrogen is discharged at the surface of the mercury. This has been proved to occur whether or not the metal is more electropositive than hydrogen in the potential series (S. W. J. Smith, *Phil. Mag.*, 1909, **17**, 834). Two extreme courses are open to this atomic hydrogen : it may wholly combine with the oxidising solution present (in which case the reducing efficiency of the metal is 100%), or it may wholly combine to form molecular hydrogen at the surface of the metal. The former course, it is expected, would be favoured by the presence of ions which are quickly reduced, and by a metal the power of which for catalysing the formation of molecular from atomic hydrogen is small; the latter course would be favoured by the presence of ions that are reduced slowly, and by a metal which catalyses the formation of molecular hydrogen. Of the three solutions tried, ferric sulphate was found by a series of comparative tests to be reduced most quickly, and uranyl sulphate most slowly, by amalgams of each of the metals investigated. Of these metals, mercury has the highest, and iron the lowest, hydrogen over-voltage, and, if this phenomenon be interpreted as the inability of the metal to catalyse the reaction $2H \longrightarrow H_2$, it follows that, of the metals under discussion, mercury does this most slowly and iron most quickly.

The experiments described above may now be explained. When potassium permanganate is reduced in acid solution, only the very reactive zinc can generate more hydrogen (or more reactive hydrogen) than can be retained at the surface of the metal until it

reacts with the permanganate. When ferric sulphate is reduced, the increased rate of reaction between it and the atomic hydrogen is sufficient to prevent any formation of molecular hydrogen; zinc is consequently, like the other metals, 100% efficient as a reducer. When uranyl sulphate is reduced, the slower rate of reaction between it and atomic hydrogen explains the smaller reducing efficiency of zinc. Comparative tests which we have made on the rate of reduction of uranyl sulphate in acid solution by amalgams of different metals, show that as the metal becomes more and more electronegative the rate at which it reduces uranyl sulphate relative to that at which it reduces permanganate decreases rapidly. Zinc, for example, reduces permanganate about 20% more rapidly than the less reactive lead under similar conditions; it reduces uranyl sulphate, however, about ten times more rapidly. These observations explain the low efficiencies of metals and their decrease with decrease in electrode potential when they reduce uranyl sulphate.

Since iron falls in the potential series of metals in mercury between copper and bismuth, it is to be expected from the results above that it would show a 100% reducing efficiency both with potassium permanganate and with ferric sulphate. The lower values found cannot be explained by supposing that the iron, which appears to be in the passive state in mercury, has become active, because there is no other evidence that iron when reducing permanganate or ferric sulphate becomes active, and further, zinc, which is 100% efficient as a reducer of ferric sulphate, is more electropositive than active iron. The explanation of the low values is that iron is the only metal in the amalgams investigated which so catalyses the reaction $2H \longrightarrow H_2$ that not all of the atomic hydrogen is used in reducing the oxidising solution. This is confirmed by the results of experiments on the reducing efficiency of zinc on permanganate in amalgams containing one other metal.

We find that cadmium, tin, and lead do not lower the reducing efficiency of zinc, that iron lowers it a little, and that tungsten, molybdenum, and platinum, which have very small hydrogen over-voltages, reduce it considerably. These experiments will be detailed in a separate communication. The following experiments lead more simply to the same result: (1) When a c.c. of $N/10$-permanganate are shaken in sulphuric acid solution with iron amalgam the permanganate is first reduced and the resulting ferric sulphate is then quantitatively reduced by more iron to the ferrous condition. When this solution is titrated with the same permanganate, it requires theoretically $a/2$ c.c., if iron has a reducing efficiency of 100%. Experimentally it requires usually from 0·2 to 0·5 c.c. in excess of this amount, showing that some of the iron

present in the amalgam has gone into solution without performing any reduction of either the permanganate or the ferric solutions present. (2) When a c.c. of $N/10$-ferric sulphate are shaken in sulphuric acid solution with iron amalgam a solution of ferrous sulphate results. This solution should theoretically require $3a/2$ c.c. of $N/10$-permanganate when titrated. Experimentally it requires from 0·2 to 0·5 c.c. in excess of this amount for the reason explained above. (3) When the same volume of the solution in (2) is shaken with a tin- instead of an iron-amalgam, ferrous sulphate and stannous sulphate but no stannic sulphate are found to form. This solution should theoretically require $2a$ c.c. of $N/10$-permanganate, since stannous sulphate and ferrous sulphate are formed in equivalent amounts. Experimentally this value is found, which shows that tin is 100% efficient in these circumstances.

From this survey it follows that, of the metals considered, iron alone cannot be directly determined in mercury by measuring the volume of potassium permanganate or ferric sulphate reduced by the metal. Owing to the rapidity of the reaction between the metal and the ferric sulphate and consequent danger of over-running the end-point, it is better to use potassium permanganate in presence of $2N$-sulphuric acid as oxidiser except when zinc is being determined. Iron may be determined easily and quantitatively by the following modification of the method. The iron amalgam is shaken with the permanganate until the end-point is obviously passed. The reduced solution is transferred to a bottle and shaken for one minute with 1% zinc amalgam. Mercury salts are thereby reduced to the metal, which dissolves in the amalgam, and iron salts are wholly reduced to the ferrous state. The liquid is then decanted from the amalgam, which is washed by decantation with two volumes of 50 c.c. of water containing dilute sulphuric acid and the whole titrated with $N/10$-permanganate.

The method described above should be a rapid and useful alternative to several more accurate but tedious processes. Three readily suggest themselves and we have carried out a few experiments on each: (1) the determination of the solubilities of metals in mercury, (2) the determination of tin and lead in solder, (3) the determination of metals electrolytically using a cathode of mercury.

Determination of Solubilities of Tin and Iron in Mercury at 15°.— To 800 g. of mercury were added 15 g. of pure tin. The solid phase was obviously present. The mixture was kept for an hour at 15° and then pressed through chamois leather three times to remove the whole of the solid phase. The amalgam was shaken with acidified permanganate in the usual way until the end-point was reached; the whole of the tin was then in solution in the

stannic form, since tin amalgam was found not to reduce stannic sulphate in measurable amount. The mass of tin in the known weight of the amalgam was then calculated from the volume and strength of the permanganate. The percentage of tin in solution in mercury at 15° was found in this way in two experiments to be 0·61 and 0·60.

A similar experiment was carried out with iron. This metal was obtained in solution by electrolysing a normal solution of ferrous sulphate containing sulphuric acid with a current of 3 amperes with a mercury cathode until the solid phase was obviously present. The solid phase was removed at 15° as with tin. Owing to the very small solubility of iron in mercury, as well as to its not being 100% efficient, the permanganate was used merely to remove the iron quantitatively from the mercury. The solution containing the iron was then treated as mentioned above and titrated with permanganate. In three experiments the solubility of iron in mercury at 15° was found to be 0·00138, 0·00140, and 0·00140%. Richards and Garrod Thomas (*Z. physikal. Chem.*, 1910, **56**, 758) found by other methods the value 0·00134 at 20°.

Determination of Tin and Lead in Solder.—The conditions necessary for success in these determinations are (*a*) that the alloy dissolves without difficulty in warm mercury, (*b*) that it has two constituents only, each of which is 100% efficient in reducing the oxidising solution used, and (*c*) that the equivalents of the metals be as widely different as possible. Solder fulfils these conditions well. A table was compiled showing the quantities of decinormal permanganate theoretically required by a gram of solder (containing lead and tin only) of varying tin composition when it is oxidised to stannic and lead sulphates. It showed that a difference in percentage composition of tin or lead of 0·1 corresponded to 0·24 c.c. of $N/10$-potassium permanganate. Since the end-point in our method can be judged with practice to about 0·2 to 0·3 c.c. of permanganate, the error of a single determination need not exceed 0·1. In practice, however, this accuracy was not always attained. In the table below, the percentage compositions of three solders obtained by the new method are compared with those determined gravimetrically.

	Percentages determined by new method.					Average values.	% determined gravimetrically.
Sn	46·4	46·3	46·5	46·3	46·4	46·4	46·4
Pb	53·6	53·7	53·5	53·7	53·6	53·6	53·6
Sn	36·4	36·3	36·1			36·3	36·1
Pb	63·6	63·7	63·9			63·7	63·9
Sn	50·7	49·8	50·0			50·2	50·5
Pb	49·3	50·2	50·0			49·8	49·5

It is seen that in the three cases the agreement is fair. A determination by the new method which includes the time taken to weigh the solder may be made in 15 minutes. We usually weighed out about 0·2 g. and this required about 60 c.c. of $N/10$-permanganate. As is to be expected from its position in the potential series, tin in the solder oxidises the permanganate before lead. This is inferred because the discoloured solution is at first clear. Later the white precipitate of lead sulphate makes its appearance. The precipitate does not obscure the end-point.

Modification of E. F. Smith's Method of Determining Metals with a Mercury Cathode.—The following metals have been found by Smith and others to be rapidly and quantitatively precipitated from solution with the use of a rotating anode and a mercury cathode : bismuth, cadmium, chromium, cobalt, copper, gold, iron, lead, manganese, mercury, nickel, silver, tin, and zinc (E. F. Smith, "Electroanalysis," 6th edition, 1919). These metals are determined by Smith's method as the difference in the weight of pure mercury before electrolysis and that of the amalgam after. With our method neither the pure mercury nor the amalgam need be weighed, so that the errors involved, especially in the second of these weighings, are avoided. On the other hand, the error of determination is greater with our method (about 0·5%) than with Smith's method when properly carried out (0·1 to 0·2%). Moreover, our method is confined to the determination of bismuth, cadmium, copper, iron, lead, manganese, tin, and zinc. The other metals named above, except chromium and cobalt, cannot be determined because they are more electronegative than mercury. Chromium cannot be determined by our method because instead of forming chromium sulphate, as is to be expected, in presence of an oxidising agent, it leaves the mercury in a finely divided state and becomes oxidised to chromous oxide. The case of cobalt has already been considered.

Rapid Method of Purifying Mercury.

A rapid method of purifying mercury from other metals may be founded on the quantitative determinations described above and is indeed obvious. It cannot be used for removing nickel or metals more electronegative than mercury, and cobalt presents some difficulty. The remaining metals more electropositive than mercury, even when in the passive state, may be removed quickly, completely, and without any loss of mercury.

If the amalgam is a concentrated one, it should be pressed twice through chamois leather to withdraw the whole of the metals in the solid phase. This lowers the concentrations of cadmium,

indium, thallium, lead, zinc, and tin to approximately 3, 2, 2, 1, 1, and 0·5%, respectively, and leaves those of copper and iron less than 0·003% (Richards and Wilson, *Z. physikal. Chem.*, 1910, **56**, 729; Richards and Garrod Thomas, *ibid.*, p. 758). The amalgam may then be placed in a stout reagent bottle and shaken vigorously with a mixture of equal volumes of 9*N*-sulphuric acid and saturated aqueous solution of potassium permanganate till it becomes discoloured. More of the oxidising solution is then added and the shaking continued till bubbles of mercury appear on the surface. The amalgam is then washed from impurities by a stream of water, and the removal of the last traces of the impure metal completed by shaking with *N*/10-permanganate acidified with 2*N*-sulphuric acid till the end-point, at which the mercury when shaken becomes a mass of small bubbles, is reached. The mercury should then be again washed by a stream of running water, shaken with 2*N*-sulphuric acid to destroy the bubbles, and pressed through chamois leather.

If *N*/10-potassium permanganate in sulphuric acid solution be used instead of the more concentrated solution the rate at which the metallic impurities are removed is slower. For small concentrations of impurities, however, this rate is not unduly slow (the removal of 0·2 g. of zinc, for example, would require about 2 minutes' shaking), and whenever the reduced solution is intended to be subsequently analysed this rate is recommended because it ensures that the end-point is not over-stepped. When the amalgam is shaken with a concentrated solution of ferric sulphate in sulphuric acid or with a mixture of this solution with permanganate, the rate at which the impurities are removed is very greatly increased. This is due to the observed fact that ferric sulphate is reduced much more rapidly than permanganate, and the greater the concentration of the ferric sulphate the more rapid is the reduction. Ferric sulphate thus catalyses the reduction of potassium permanganate and other oxidising solutions by amalgams because the former after reduction to ferrous sulphate reacts almost instantaneously with the latter and the ferric sulphate regenerated is then reduced by more of the metal of the amalgam. Using a normal solution of ferric sulphate in 2*N*-sulphuric acid, we were able, by vigorous shaking, to remove 1 g. of lead from 200 g. of amalgam in 10 seconds, and 7 g. of zinc in ½ minute. With a concentrated solution of permanganate in 6*N*-sulphuric acid and 20 c.c. of *N*/10-ferric sulphate we removed completely, by shaking in a large reagent bottle, 14 g. of a mixture of zinc, cadmium, tin, lead, solder, and bismuth from 480 g. of pure mercury, to which it had been added, without the loss of any mercury except a little removed

mechanically in washing. This fact is of interest because in the literature on the purification of mercury it is stated that when an amalgam is passed through, or shaken with, the oxidising solutions in general use, either the mercury is not completely freed from the more electropositive metals or, if it is, a considerable proportion of mercury accompanies the other metals into solution (Harries, *Z. angew. Chem.*, 1921, **34**, 359; Harries and Evers, *ibid.*, p. 541; Hulett and Minchin, *Physical Rev.*, 1905, **21**, 396).

Summary.

1. The order in which metals are removed from mercury by oxidising solutions has been determined, and is given but not discussed.

2. The reducing efficiency of amalgams of zinc, cadmium, tin, lead, copper, iron, and bismuth has been determined in solutions of ferric sulphate, potassium permanganate, and uranyl sulphate containing dilute sulphuric acid. The results are interpreted in terms of the hydrogen over-voltages of these metals.

3. The results are applied to rapid, approximate methods of determining (*a*) the solubilities of metals in mercury, (*b*) tin and lead in solder, (*c*) metals deposited by electrolysis with a rotating anode and a mercury cathode.

4. A rapid method of purifying mercury from more electropositive metals by shaking the amalgam with an oxidising agent is described. It removes such metals completely without necessarily the loss of mercury. The rate at which this purification is done may be regulated.

We wish to thank the Government Grant Committee of the Royal Society for providing us with the materials employed in this work.

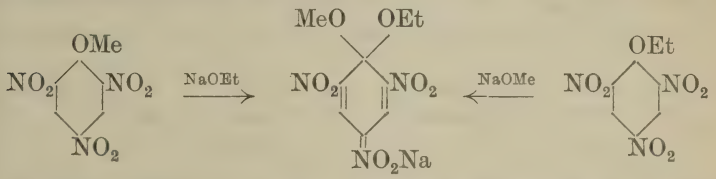
DR. LEE'S LABORATORY,
CHRIST CHURCH, OXFORD. [*Received, July 10th*, 1925.]

CCCII.—*The Alcoholysis of Trinitroanisole and Trinitrophenetole.*

By OSCAR L. BRADY and HAROLD V. HORTON.

IN connexion with other investigations it had been found that when 2 : 4 : 6-trinitro-*m*-tolyl methyl ether was crystallised from alcohol, partial conversion into the corresponding ethyl ether occurred and that when 3 : 5-dinitro-*o*-tolyl methyl ether was heated with

alcohol in the presence of alkali a similar change took place. The behaviour of 2 : 4 : 6-trinitroanisole and trinitrophenetole has now been investigated. Meisenheimer (*Annalen*, 1902, **323**, 205) has shown that the same compound is obtained by the action of sodium ethoxide on trinitroanisole and of sodium methoxide on trinitrophenetole and that this compound on decomposition with acids gives a mixture of trinitroanisole and trinitrophenetole; he proposed the following mechanism :



Similarly, Loving, Jackson, and Boos (*Amer. Chem. J.*, 1898, **20**, 444) found that when the compound obtained by the action of sodium methoxide on trinitroanisole was crystallised from ethyl alcohol, substitution of ethyl for methyl took place. Purdie and Marshall (J., 1888, **53**, 391) observed that a change of groups occurred between esters of carboxylic acids and alcohol in the presence of a small amount of sodium. The conversion can, in some cases, be carried out without the addition of sodium (Shimomura and Cohen, J., 1922, **121**, 883, 2051; see also Cohn, *Monatsh.*, 1900, **21**, 200; Lapworth and Havin, J., 1902, **81**, 1501).

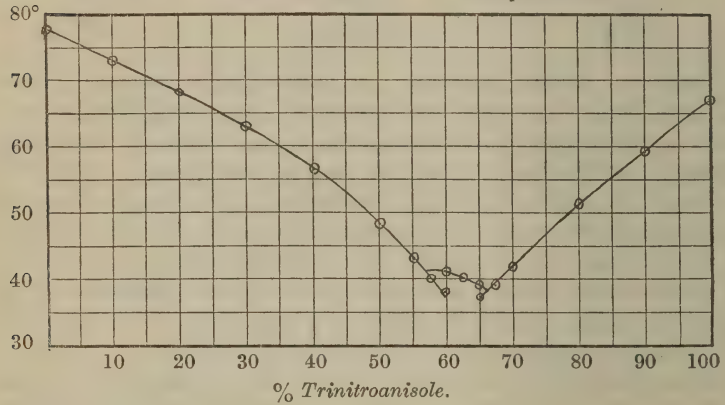
When 2 : 4 : 6-trinitroanisole (m. p. 68°) is crystallised from ethyl alcohol, a mixture, m. p. 58°, of trinitroanisole and trinitrophenetole separates, whilst trinitrophenetole crystallised from methyl alcohol gives a mixture, m. p. 52°. These observations probably account for the different values given for the melting point of trinitroanisole, namely, 48° to 64°. We have found that trinitroanisole, crystallised from dry methyl alcohol, melts in a capillary tube at 68° and freezes in bulk at 67·0°. For the purpose of analysis the binary fusion diagram of trinitroanisole and trinitrophenetole has been constructed (Fig. 1).

The two substances apparently form an unstable addition compound consisting of 3 mols. of trinitroanisole and 2 mols. of trinitrophenetole, corresponding with 58·7% of trinitroanisole. This compound does not separate readily and it is possible to prolong the left and right branches of the curve for some distance into the metastable region; in taking the time–cooling curve of a mixture containing 60% of trinitroanisole, trinitrophenetole separates at 38·0°, the temperature remains constant for some time and then rises to 41·0°, when the additive compound separates.

When a mixture of trinitroanisole (1 mol.) and absolute alcohol (10 mols.) was evaporated in an air-oven, and the residue dried at 100°, irregular results were obtained, the product having a freezing point of from 38·4° to 42·3°; it was found that picric acid had been formed owing to absorption of water by the alcohol during working. An apparatus was therefore designed in which the alcohol was distilled from calcium oxide directly on to the trinitroanisole in the vessel in which the freezing point was ultimately to be determined, the whole apparatus being filled with dry air; the mixture was then heated in an oil-bath, finally to 150°, a current of dry air being passed

FIG. 1.

2 : 4 : 6-*Trinitroanisole*–2 : 4 : 6-*Trinitrophenetole*.



over it to remove alcohol vapour. Since two layers formed as the alcohol evaporated, the mixture was stirred continuously. By this means it was found that in mixtures of alcohol and trinitroanisole in the molecular proportions of 11 to 1 and 16 to 1 conversion occurred to the extent of 16% and 22% respectively; with larger amounts of alcohol, the results were irregular, but even with 68 mols. not more than 35% of the trinitroanisole was converted into trinitrophenetole.

EXPERIMENTAL.

Preparation of Materials.—2 : 4 : 6-Trinitroanisole was prepared by two methods. 2 : 4-Dinitroanisole, prepared by the action of sodium methoxide in methyl alcohol on 2 : 4-dinitrochlorobenzene, was nitrated by Holleman's method (*Rec. trav. chim.*, 1903, 22, 263), the nitrating mixture being heated for 3 hours at 100° and the product crystallised from methyl alcohol. Picryl chloride was treated in boiling methyl alcohol with sodium methoxide (1 equiv.) in the same

solvent, a fresh addition not being made until the colour produced by the last had almost faded. When all the sodium methoxide had been added, the mixture was diluted somewhat with water; the trinitroanisole that separated on cooling was crystallised twice from dry methyl alcohol and thus obtained pure (m. p. 68°).

Attempts to nitrate 2 : 4-dinitrophenetole to trinitrophenetole under various conditions were unsuccessful, hydrolysis occurring and picric acid being the only product isolated. Trinitrophenetole was therefore prepared from picryl chloride by the action of sodium ethoxide in a similar way to trinitroanisole (Austen, *Ber.*, 1875, **8**, 666). After experiments with thionyl chloride had proved unsuccessful, picryl chloride was prepared by a modification of Pisani's method (*Annalen*, 1854, **92**, 326). Picric acid (50 g.; larger quantities cannot safely be employed) was mixed with phosphorus pentachloride (100 g.) and heated under reflux on the water-bath. After the violent reaction had subsided, the product was poured into water and rapidly collected. After air-drying, the crude material was purified in lots of 20 g. by heating at 100° for some time with a mixture of one part of nitric acid (*d* 1·4) and four parts of sulphuric acid (*d* 1·8), cooling, pouring into water, and crystallising from a mixture of benzene and alcohol (1 : 3). The yield of pure product was about 50% of that calculated.

The freezing points of mixtures of trinitroanisole and trinitrophenetole were determined from time–cooling curves; the results are in Table I.

TABLE I.

% Trinitroanisole	0	10	20	30	40	50	55	56	57·5
F. p.	77·6°	72·6°	67·9°	62·9°	56·4°	48·1°	43·0°	42·0°	40·1°
% Trinitroanisole	60	62·5	65	67·5	70	80	90	100	
F. p.	41·0° (38·0°)	40·3°	39·4° (37·3°)	39·2°	41·7°	51·0°	59·3°	67·0°	

The figures in brackets correspond to the first arrest, where the trinitroanisole or trinitrophenetole first separated and crystallisation of the compound followed.

In conclusion, one of us (H. V. H.) wishes to thank the Department of Scientific and Industrial Research for a grant which has enabled him to take part in this work.

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CCCIII.—*The Supposed Formation of* 1:2:4-*Oxadiimine Rings from Nitroso-compounds and Methyleneарylamines.*

By GEORGE NORMAN BURKHARDT, ARTHUR LAPWORTH, and EDWIN BREW ROBINSON.

INGOLD prepared a number of compounds by the action of nitrosobenzenes on methyleneanilines (J., 1924, **125**, 93 *et seq.*). He ascribed to the products a ring structure, $ArN<^{CH_2}_{-O-}>NAr'$, and asserted that the facts were totally contrary to "the hypothesis by means of which so many obscure facts in chemistry are nowadays 'explained'" (*loc. cit.*, p. 93).

He subsequently discovered that his products were not ring compounds at all, but *N*-hydroxyamidines. In a paper with Farrow (J., 1924, **125**, 2543), he maintained, nevertheless, that cycloids are formed in the first instance and that these cycloids isomerise to hydroxyamidines at the moment of their formation (*loc. cit.*, p. 2545):

$$\left.\begin{matrix}CH_2{:}NAr\\ O{:}NAr'\end{matrix}\right\} \rightarrow ArN<^{CH_2}_{-O-}>NAr' \leftarrow \left\{\begin{matrix}CH_2{:}NAr'\\ O{:}NAr\end{matrix}\right.$$

$$\downarrow$$

$$ArN(OH)\cdot CH{:}NAr'$$

The proof given was that "the substances obtained in the two ways shown by the equation above are, in each case, identical with one of the pair of isomerides prepared by Comstock and Clapp's reaction."

Only one such case, however, was described, namely, that where $Ar = C_6H_4Br(p)$ and $Ar' = C_6H_4Cl(p)$ (Ingold, *loc. cit.*, p. 101), an unsatisfactory pair in view of the close chemical relationship and likely isomorphism of their derivatives.

Farrow and Ingold also referred to the case where $Ar = C_6H_5$ and $Ar' = C_6H_4\cdot CH_3(p)$; but here the product was made in only one of the ways indicated in the above scheme, namely, from $CH_2{:}N\cdot C_6H_4\cdot CH_3(p)$ and $O{:}N\cdot C_6H_5$. It is most significant that the product was identified with $N(C_6H_4\cdot CH_3){:}CH\cdot N(C_6H_5)\cdot OH$, which on alkaline hydrolysis gave *azoxybenzene* with no trace of azoxytoluene (*loc. cit.*, p. 2551—2552) and *p*-toluidine. Here, be it noted, the aromatic radical in the original *nitroso*-compound reappears in attachment to *oxidised nitrogen* and the other, originally as methylene*amine*, as pure amine with *unoxidised nitrogen*.

Returning to the crucial case where $Ar = C_6H_4Br$ and

$Ar' = C_6H_4Cl$: a product A, made from chloronitrosobenzene and methylenebromoaniline, was identified with another, B, made from bromonitrosobenzene and methylene-*p*-chloroaniline (Ingold, *loc. cit.*), and both with a third product, C, which was made in quite a different way and certainly had the structure

$$C_6H_4Cl\cdot N(OH)\cdot CH{:}N\cdot C_6H_4Br.$$

The last-mentioned gave pure *p*-bromoaniline when hydrolysed by alkali (Farrow and Ingold, *loc. cit.*, 2551, 2552).

The present authors had good theoretical reasons for thinking it unlikely that such a ring would be formed at all in the addition process, and still more unlikely that such a ring, once formed, would break down exclusively in one direction. They therefore took up the re-examination of the product obtained by Ingold's method from *p*-chloromethyleneaniline and *p*-bromonitrosobenzene. Observing that, even after recrystallisation from benzene, the product was not very well defined, and remembering that it might be isomorphous with its isomeride (from which it differs only in the interchange of place of chlorine and bromine), they decided to hydrolyse it with aqueous-alcoholic sodium hydroxide in the general way described by Farrow and Ingold (*loc. cit.*, pp. 2547, 2548) and to examine the substituted aniline so formed. The resulting base solidified at once; even before recrystallisation it melted 67—69°, and after one crystallisation from light petroleum at 68·5—69°. (A sample of pure *p*-chloroaniline obtained from British Drug Houses Limited melted after similar treatment at 69·5—70°; and a sample of pure *p*-bromoaniline after similar treatment at 62—62·5°.)

We are indebted to Dr. E. Chapman, who has had much experience in the determination of halogen by Robertson's method, for an analysis of the base. 0·1068 Gram of the compound gave halogen equivalent to 8·23 c.c. of $N/10$-$AgNO_3$. Formula C_6H_6NCl requires 8·37 c.c. and C_6H_6NBr requires 6·21 c.c.

It is thus clear that the base was mainly *p*-chloroaniline; the authors thought they detected a very small quantity of bromine in a careful qualitative test, but this would not be very surprising, as some reduction of the bromoazo-compounds during the original hydrolysis seemed quite possible.

It is evident that a compound which yields mainly *p*-chloroaniline cannot possibly be identical with one which, as Farrow and Ingold stated, yields *p*-bromoaniline with no trace of *p*-chloroaniline. That such a mistake could ever have been made is proof that the evidence on which Ingold relied was not trustworthy and it cannot be admitted that there is any good reason to suppose that his cycloids are formed at any stage.

If Farrow and Ingold are disposed to maintain their original view, then the onus of proof rests with them. An obvious and acceptable line of proof would be for them to prepare their compounds by both the methods in the scheme on p. 2234 and to show that these then give the same products in the same proportion when hydrolysed.

In conclusion, the facts, so far as they have yet been fully established, are entirely consistent with polarity theories, all previous statements to the contrary notwithstanding (*inter alia*, Ingold, J., 1924, **125**, 93; Ingold and Weaver, *ibid.*, pp. 1457—1459).

THE UNIVERSITY, MANCHESTER. [*Received, June 18th*, 1925.]

CCCIV.—*The Properties and Constitution of Coal Ulmins. Studies in the Composition of Coal.*

By WILFRID FRANCIS and RICHARD VERNON WHEELER.

WE have demonstrated (this vol., p. 112) that bituminous coal consists essentially of a matrix of insoluble ulmins in which morphologically organised plant tissues and natural plant-substances devoid of morphological organisation, that have escaped ulmification, are dispersed; * thereby confirming conclusions reached from other considerations (Tideswell and Wheeler, J., 1922, **121**, 2345; 1925, **127**, 110). In some bituminous coals the proportion of plant entities, chiefly cuticles and spore exines, is as high as 20% by weight, but in all bituminous coals the ulmins form the predominant material. Knowledge of their properties and constitution is therefore essential to an understanding of the composition of coal. We have sought to obtain this knowledge by both synthetic and analytical means. The present paper deals with the results of our analytical studies.

The chief effect of mild oxidation on bituminous coal is to change the matrix of ulmins from a form insoluble in dilute alkalis to a soluble form, thereby allowing of their separation from the organised plant material associated with them and rendering possible their examination by the usual methods of organic analysis. Suitable

* The matrix is not structureless, as was originally supposed, but close examination discloses, even in material selected as being a vitrain, a more or less pronounced structure, usually of woody tissue, such as a theoretically perfect vitrain should not possess. Such structures cannot, however, be separated from the coal mass intact, as can the cuticles and spore-exines, and they are ulmified.

mild oxidation can be effected by such reagents as hydrogen peroxide, or by exposure to air at 150°.

No fundamental change in the structure of the ulmin molecule is made by such a mild oxidation, but the external groupings are modified, those most readily detached being eliminated as simple oxygenated compounds and their place being taken by carboxylic groupings. The internal or nuclear arrangement of the molecule of the soluble " regenerated " ulmin (*loc. cit.*, p. 123) is thus identical with that of the insoluble matrix of unoxidised bituminous coal, and from a knowledge of the constitution of the former the essential structure of the main mass of bituminous coal can be deduced.

The change from insoluble to soluble ulmins is a gradual one. A moderate degree of oxidation will produce sufficient change in the external groupings of the ulmin molecule to render the matrix of bituminous coal soluble with difficulty in alkalis. As oxidation proceeds, more groupings are eliminated and the ulmins become more acidic in character and more readily soluble in alkaline or neutral solvents. A limiting condition is, however, eventually reached when all suitable external groupings have been eliminated. (In this connexion, compare Pearson, *J. Soc. Chem. Ind.*, 1923, **42**, 68T.) This stage is reached on oxidation by air at low temperatures. Further, carefully regulated, oxidation by hydrogen peroxide or nitric acid can cause a breakdown of the nuclear structure of the ulmin molecule and it is by the identification of any simpler compounds resulting from such a breakdown that the character of the nucleus of the complicated ulmin molecule can be revealed.

The Properties of Regenerated Ulmins.—Because the changes produced in bituminous coal by mild oxidation are gradual, the soluble ulmins produced are not homogeneous. They can be separated into a number of fractions by means of different solvents; but all the fractions are compounds of the same type and differ but slightly one from another in their analysis. We have not considered it necessary to effect a separation of them for the major portion of the work described in this paper.

The carboxyl groups produced by oxidation give to the soluble ulmins a definite acidic character allowing of salt formation. Amongst the insoluble salts that we have prepared are those of barium, iron, silver and copper. From the last-named an average value of 170 for the equivalent of the ulmins has been obtained, a figure which should be compared with that given by Sven Odén, namely, 350, for soil ulmins (*Proc. Faraday Soc.*, 1921). No convenient method is at present available for determining the molecular weight (if the colloidal character of the substances admits of such

a determination), but from the value of the equivalent an expression can be given of the contents of such determinable groupings as hydroxyl and carboxyl, and of nitrogen. The presence of hydroxyl groups has been proved by acetylation and benzoylation and by Grignard's reaction. By hydrolysis of the acetyl derivatives the percentage of hydroxyl groups in the " regenerated " ulmins as an average has been found to be 2·5, or one hydroxyl group for each molecular unit of 680. Such a unit would contain four carboxyl groups, a supposition confirmed by a quantitative estimation of the methane evolved from the dry ulmin on treatment under suitable conditions, with Grignard's reagent.

It is significant that as the oxidation of coal proceeds, with the gradual formation of soluble ulmins, the nitrogen-content increases up to the point at which the whole of the coal matrix becomes soluble. Moreover, all the slightly modified types of regenerated ulmins that can be separated by means of organic solvents contain nitrogen in the same proportion. This element must therefore be an essential constituent of the nucleus of the ulmin molecule.* The percentage of nitrogen found, 2·20—2·25, would indicate the presence of one nitrogen atom in the molecular unit suggested.

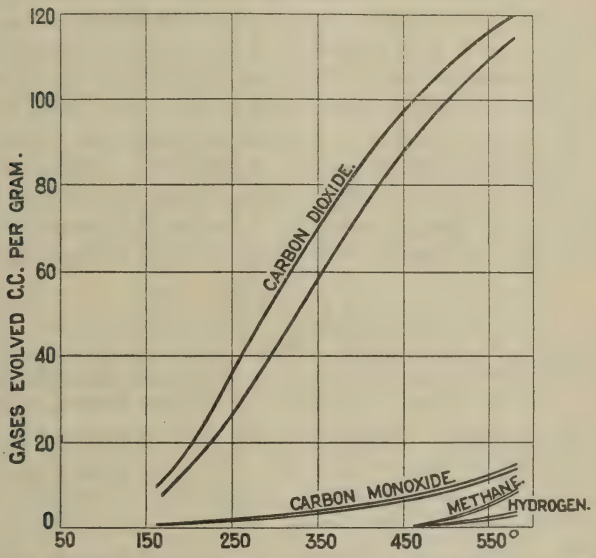
The presence of nitrogen as an essential constituent of the molecule renders it necessary to take account of this element in any theory regarding the origin of the coal-ulmins and lends particular interest to the reaction between amino-acids and sugars discovered by Maillard (*Ann. Chim. Phys.*, 1916, **5**, 258; 1917, **7**, 113) which results in the formation of ulmins. In the coal-forming process, from plant debris, the sugars may be derived from the celluloses of the cell-walls by enzyme or bacterial action and the amino-acids from the polypeptides in the protein matter of the cell contents. These reactions, whereby it is conceivable that the matrix of coal can be synthesised, are being studied by Mr. T. A. Buckley.

Some information as to the character of the external groupings of the molecule of the regenerated ulmin is given by the results of regulated destructive distillation. On heating the ulmins in the manner described in the experimental portion of this paper, gas began to be evolved in small quantity at 160—170°. This gas consisted of the oxides of carbon in ratio CO_2/CO of 12 : 1. This ratio increased up to 300° and then rapidly decreased. Measurable quantities of hydrogen and saturated hydrocarbons were not evolved until about 450°. Water accompanied the oxides of carbon at the lower temperatures of distillation, but no other

* A similar conclusion is to be drawn from the experiments of Monkhouse and Cobb (*Trans. Inst. Gas. Eng.*, 1922) on the action of steam on coke.

liquid made its appearance until 550°, when a slight trace of oil could be detected. These results correspond in general character with those obtained with the peat ulmin, dopplerite (Tideswell and Wheeler, J., 1922, **121**, 2345). The striking similarity of the curves relating the evolution of gases with temperature (Fig. 1), obtained with ulmins prepared from a vitrain and a durain respectively, confirms the deductions previously made (*loc. cit.*) that the matrix of a durain is essentially the same as that of a vitrain (or a clarain), differing from it only as regards the character of the less important external groupings of the molecules.

FIG. 1.



Destructive distillation of regenerated ulmins. For each gas the upper curve relates to a vitrain ulmin and the lower to a durain ulmin.

The Constitution of the Regenerated Ulmins.—By breaking down the nucleus of the molecule, by the cautious use of hydrogen peroxide or dilute nitric acid, simpler compounds can be obtained, the identification of which gives information as to the groupings within the nucleus. A number of such compounds have been identified.

The extreme action of hydrogen peroxide on the regenerated ulmins results in the formation of water and the oxides of carbon, the nitrogen appearing quantitatively as ammonia. Intermediate action yields aliphatic dibasic acids, of which oxalic and succinic have been isolated in pure crystalline form, together with a number of acids having all the properties of benzene polycarboxylic acids.

The isolation and identification of all these acids can, however, more readily be effected by the use of dilute nitric acid, which yields water-soluble products, amounting to about 25% of the regenerated ulmin, consisting of aliphatic dibasic acids, aromatic acids and nitrophenols. The products so far isolated and identified are oxalic, succinic, picric and pyromellitic acid (benzene-1 : 2 : 4 : 5-tetracarboxylic acid), whilst there is evidence of the presence of trimellitic acid. (Fischer and Schrader, *Brennstoff-Chem.*, 1921, **2**, 213, obtained traces of aromatic carboxylic acids by the pressure oxidation of a bituminous coal at 200—250°.)

The identification of picric and pyromellitic acids proves beyond question the presence of benzenoid rings in the nucleus of the regenerated ulmin molecules, and hence in the matrix of bituminous coal, for no part of our treatment of the coal has been such as to cause ring formation where none previously existed. Since such aliphatic acids as oxalic and succinic have also been obtained, whilst the nitrogen is clearly present in stable ring formation, it can be concluded that the nuclei of the ulmin molecules—which form the bulk of all bituminous coals—consist of compact systems of benzenoid groupings connected together by heterocyclic ring structures, such as pyrrole and furan or their derivatives.

Experimental.

Preparation of Regenerated Ulmins from Bituminous Coal.—A vitrain was usually employed so as to avoid the complications introduced by the presence of plant debris and to obtain the maximum yield of ulmins. The vitrain was finely ground and added to three times its weight of 100 vol. hydrogen peroxide. After a few minutes the mixture began to rise in temperature and the reaction tended to become violent. To moderate it, cold distilled water was added. The mixture was then heated at about 90° during several hours. The soluble ulmins thus formed were extracted with dilute sodium hydroxide solution and the residue was re-treated with hydrogen peroxide, the processes being repeated until no residue remained.

As thus prepared, soluble ulmins from the vitrain of East Kirkby coal contained C 68·8 and H 3·9%. Successive treatments of this material with hydrogen peroxide caused a reduction in the carbon and hydrogen contents until a limiting composition C 62·5 and H 2·8% was reached, similar figures being obtained with all the coals examined (whether vitrains, clarains, or durains). In obtaining this limiting composition, however, some destruction of the ulmins occurred and, since for subsequent examination a large yield rather than a homogeneous material was required, the usual

procedure was to check the oxidation as soon as solubility was attained.

Solubility of the Regenerated Ulmins.—The non-homogeneous ulmins so obtained were fractionated by means of solvents and each fraction was examined separately. The solvents used, at their respective boiling points, were : Chloroform, ethyl alcohol, acetone, methyl ethyl ketone, pyridine, pentane, light petroleum, benzene, ether, and carbon disulphide. Only the first five of these had any marked solvent action. In Table I the percentage amounts extracted by each solvent, in the order named, from a number of samples of regenerated ulmins are recorded.

TABLE I.

Solubility of Regenerated Ulmins.

	Source of Regenerated Ulmin.					
	East Kirkby vitrain.			East Kirkby vitrain α-compounds.*		
Solvent.	Sample A.	Sample B.	East Kirkby durain.	Sample A.	Sample B.	Hamstead vitrain.
Chloroform	0·4	0·4	0·3	0·4	—	—
Alcohol	7·2	2·2†	7·5	6·4	40·2	28·0
Acetone	3·8	12·2†	4·5	5·4	9·0	5·0
Me Et ketone ...	—	4·3	—	—	—	—
Pyridine	33·0	42·0	38·5	36·0	23·0	19·5

* The term α-compounds refers to that portion of the coal that was insoluble in pyridine.

† Order of extraction reversed.

All the ulmins, except sample B from the East Kirkby vitrain α-compounds and the sample from the Hamstead vitrain, were obtained as soon as the treatment with hydrogen peroxide rendered the coals soluble in alkalis. The two exceptions were subjected to more prolonged oxidation. Analyses of many of these fractions are given in Table II.

TABLE II.

Analyses of Fractionated Ulmins. Per cent. on ash-free dry material.

Fraction. Ulmins prepared from :		Carbon.	Hydrogen.	Oxygen and nitrogen (by difference).
East Kirkby vitrain,	alcohol-sol.	64·4	5·1	30·5
,, ,,	acetone-sol.	66·6	4·9	28·5
,, ,,	pyridine-sol.	68·3	4·5	27·2
,, ,,	α-compounds alcohol-sol.	65·5	4·8	29·7
,, ,,	α-compounds acetone-sol.	65·6	4·6	29·8
Hamstead vitrain,	alcohol-sol.	63·8	4·1	32·1
,, ,,	pyridine-sol.	65·5	3·7	30·8

It will be seen that the compounds were all of the same type, the different degrees of solubility being caused presumably by slight modifications in the external groupings of the molecules. The amount extracted by each solvent depended upon the order of extraction and each fraction was to some extent soluble in the other solvents. In general it was found that the further oxidation with hydrogen peroxide had been carried the more soluble in such neutral solvents as alcohol and acetone were the products.

The Preparation of Salts and Determination of the Equivalent.—Well-defined salts of barium, calcium, silver and copper were formed by the addition of a soluble salt of the metal to an ammoniacal solution of the ulmin. The copper salt was used to determine the equivalent. For its preparation, excess of a boiling ammoniacal solution of copper hydroxide was added to the boiling ulmin solution, the mixture well stirred and allowed to cool. The precipitate, which formed readily, was washed several times by decantation, filtered off and washed free from copper hydroxide with dilute ammonia and finally with distilled water. The equivalent was calculated from the analysis of the dried salt and found to be : East Kirkby vitrain ulmin, 171 ; East Kirkby vitrain ulmin, fraction insoluble in pyridine, 164 ; East Kirkby vitrain α-compound ulmin, 165.

Examination for Hydroxyl and Carboxyl Groups.—The presence of these groups in the regenerated ulmins was proved by the formation of an acetyl derivative, using acetic anhydride and sodium acetate, and by the formation of a benzoyl derivative, using benzoyl chloride in pyridine solution. The acetyl derivative was used to estimate the content of hydroxyl by determining the amount of acetic acid liberated on hydrolysis and steam distillation with benzenesulphonic acid. The ulmin from Hamstead vitrain was found to contain hydroxyl equivalent to 2·6% ; and that from the East Kirkby vitrain 2·4%.

Estimation of the total hydroxyl, including that in carboxyl groupings, was made by the use of Grignard's reaction, 13·4% being found ; whence the number of carboxyl groups is four times that of free hydroxyl groups. As was to be anticipated, methoxyl groups were not present.

Nitrogen Content.—During the production of regenerated ulmins by atmospheric oxidation there was a gradual increase in the nitrogen content of all the coals examined until a proportion of 2·25% was reached. This figure was confirmed on analysis of the ulmins produced by the action of hydrogen peroxide. From whichever coal they were formed, and whichever solvent fraction was taken, the nitrogen content was about 2·25%. From this it

appears that most of the nitrogen of the ulmins (and of coal) resides in the nuclear groupings, which mild oxidation does not attack. Moreover, since there must be at least one nitrogen atom per molecule, it follows that the average molecular weight of the regenerated ulmin is not less than about 680. Suitable tests showed that the nitrogen was present in limited amount (not more than about 0·2%) as $-NH_2$ and $-N{\cdot}CH_3$, but the greater proportion was inert, suggesting that its chief mode of occurrence is in a closed ring compound. On the complete breakdown of such a ring, by the extreme action of hydrogen peroxide, the nitrogen is evolved quantitatively as ammonia.

Destructive Distillation.—One gram of the regenerated ulmins prepared from the East Kirkby vitrain and durain respectively was destructively distilled in a horizontal glass tube attached to a Sprengel mercury pump. The temperature was raised by stages of 50°, each temperature being maintained constant during 24 hours or until all gas had ceased to be evolved. The results of examination of the gaseous products are recorded in Tables III and IV.

Explosion analysis in each instance showed the paraffin hydrocarbon present to be methane only.

In Fig. 1 the volumes of the principal gases evolved per gram of material are plotted against temperatures of decomposition. These curves should be compared with that obtained by Tideswell and Wheeler (*loc. cit.*) on the destructive distillation of the peat ulmin, dopplerite.

Oxidation of Regenerated Ulmins.—The action of hydrogen peroxide on the regenerated ulmins was in some instances continued with the intention of breaking down the nucleus of the large ulmin-molecule, so as to obtain compounds of smaller molecular weight from which the internal structure of the ulmins could be deduced. The intense action of hydrogen peroxide was difficult to regulate, resulting most often in the production of water, ammonia and the oxides of carbon, many compounds, the isolation of which would have been of value, having only a transient existence. Nevertheless, good yields of oxalic and succinic acids were obtained and separated by fractional crystallisation. Other crystalline products, apparently polybasic acids, await identification. In addition, small quantities of acids have been obtained having all the properties of benzene polycarboxylic acids.

A more satisfactory reagent with which to effect the breakdown of the regenerated ulmin molecule, since its action could more readily be controlled, was found to be 30% nitric acid. The reaction was carried out in a flask with reflux condenser, at first without external heat and later by boiling during 12 hours. The soluble products

Table III.

Destructive Distillation of Regenerated Ulmins from East Kirkby Vitrain.

(One gram of material, containing 2·1% of ash.)

Temperature range	15—160°	160—210°	210—260°	260—310°	310—360°	360—410°	410—460°	460—510°	510—580°
Volume of gas evolved (c.c. at N.T.P.)	10·25	12·25	20·0	18·5	16·15	15·5	14·5	19·5	20·5
Analysis % :									
CO_2	92	91·3	94·6	94·7	91·2	88·4	83·9	61·9	40·4
CO	8	7·8	4·8	4·8	6·8	8·5	10·8	16·2	18·6
C_nH_{2n}	—	—	—	—	2·0	0·2	0·7	1·4	0·2
C_2H_4	—	—	—	—	—	0·5	0·9	1·6	0·4
H_2	—	—	—	—	—}	2·4	{0·8	4·8	11·5
CH_4	—	—	—	—	—}		{3·0	14·1	28·9

Table IV.

Destructive Distillation of Regenerated Ulmins from East Kirkby Durain.

(One gram of material, containing 2·5% of ash.)

Temperature range	15—170°	170—220°	220—270°	270—320°	320—370°	370—420°	420—470°	470—520°	510—580°
Volume of gas evolved (c.c. at N.T.P.)	8·2	8·6	14·5	16·0	20·0	14·5	18·0	18·5	20·0
Analysis % :									
CO_2	93	92·6	94·2	93·8	90·4	89·4	82·0	69·0	47·4
CO	7	6·9	5·4	5·2	7·4	8·3	11·6	14·5	18·2
C_nH_{2n}	—	—	—	—	0·2	0·4	0·5	1·5	—
C_2H_4	—	—	—	—	0·5	0·6	1·2	0·4	—
H_2	—	—	—	—}	1·4	1·3	{0·4	3·2	7·0
CH_4	—	—	—	—}			{4·2	11·4	27·4

were then distilled in steam, the distillate containing acetic acid. The residue was heated on a water-bath to remove the last traces of nitric acid, the product thus obtained being a pale yellow, spongy mass, completely soluble in ether and amounting to about 25% of the original ulmin. By benzene extraction, picric acid, 3% on the original ulmin, was obtained, its identification being effected by the method of mixed melting points and by the preparation of a naphthalene derivative, m. p. 149°.

By means of their lead, silver and barium salts the remainder of the soluble products of the action of nitric acid on regenerated ulmins were separated. Oxalic acid was obtained in pure crystalline form, whilst other products, nearly pure but difficult to crystallise, were benzene tri- and tetra-carboxylic acid. Symmetrical benzene-tetracarboxylic acid (m. p. 264°, with decomposition) has been isolated in a pure form by slow crystallisation from acetic acid, and its methyl ester, m. p. 138°, formed. The tricarboxylic acid appears to be trimellitic acid, but it has not yet been obtained in sufficiently pure crystalline form to identify.

The presence of picric acid and these benzene polycarboxylic acids in the products, whilst proving the existence of aromatic nuclei in coal, does not necessarily confirm the theory of Fischer and Schrader (*Brenn. Chem.*, 1922, **3**, 161) as to the origin of coal exclusively from lignin; for Marcusson's explanation (*Ber.*, 1921, **54**, 542) of the formation of ulmins from sugars through furfural as an intermediary equally allows of there being benzene nuclei in the products, the condensation of the furfural derivative to a *peri*difuran compound resulting in a substance containing both furan and six-membered rings.

The work of isolating further compounds resulting from the breakdown of regenerated ulmins from bituminous coal is being continued. Our thanks are due to the Safety in Mines Research Board for permission to publish these results.

Safety in Mines Research Board Laboratories,
Sheffield. [*Received, July 25th*, 1925.]

CCCV.—*The Coagulation of a Colloidal Solution by Hydrogen Ions.*

By Alan B. Weir.

Investigations have been recently carried out in America into one of the chief problems met with in the study of the precipitation of suspensions, emulsions, and colloidal solutions by electrolytes;

namely, whether the active agent is the ion carrying a charge of sign opposite to that of the colloid particles, or whether there is a peptising or stabilising effect due to the other electrolyte ion, the charge of which is of the same sign as that carried by the colloid.

Tartar and Gailey (*J. Amer. Chem. Soc.*, 1922, **44**, 2212) studied the precipitation of gamboge and mastic suspensions, in the first case by acids. These are negative suspensions, and the active agent should therefore be the hydrogen ion. The minimum concentration of acid for complete precipitation of the suspensions was found in the case of five acids : hydrochloric, sulphuric, oxalic, acetic, and phosphoric. The amounts of acid required differed considerably from acid to acid, but the hydrogen-ion concentration of the supernatant liquid, *i.e.*, of the medium from which coagulation had just taken place was, " within the limits of experimental error," the same in each case. The conclusion drawn from these and further experiments described in the same paper was that the " so-called stabilising effect " of the anion (on negative suspensions) could not be detected, and, further, that the irregularities often attributed to this effect were due, even in the case of coagulation by neutral salts, to the important factor of hydrogen-ion concentration.

Bradfield (*J. Amer. Chem. Soc.*, 1923, **45**, 1243), using a clay suspension, confirmed these results for several acids, which precipitated at an almost uniform p_H of 3·8, but found that citric acid was consistently abnormal, requiring a p_H of 3·2.

The author has therefore investigated the applicability of this rule to a true colloidal solution of negative sign, noting whether the abnormality of citric acid recurred.

Experimental.

The sol chosen was one of Prussian blue, as preliminary work on various arsenious sulphide sols showed that they could not be completely precipitated either with citric or acetic acid.

The sol was prepared by slowly adding 0·4 g. of potassium ferrocyanide, dissolved in 20 c.c. of water, to 0·4 g. of ferric chloride in 20 c.c. of water, filtering off the dye, washing, peptising with a solution of oxalic acid (16 g. in 300 c.c. of water), and dialysing till free from oxalic acid. The sol was then diluted to 700 c.c.

Procedure.—The precipitation of the sol by four acids, hydrochloric, sulphuric, acetic, and citric, was examined. The minimum concentration of each acid required for complete coagulation of the sol was found in the usual manner. Graded amounts of the stock acid solutions were placed in test-tubes and accurately diluted to 10 c.c., then 10 c.c. of the sol were added, the whole was mixed

by pouring, and kept for 48 hours (for this sol flocculates slowly). The amounts of the acids required (per 20 c.c. of mixture) were thus found with an accuracy of 0·1 c.c.

In the case of the four critical concentrations, the supernatant liquid, after the dye had been precipitated, was poured off, and its hydrogen-ion concentration ascertained by means of a Clark hydrogen electrode. For standards, saturated and $N/10$-calomel electrodes were used.

In order to see whether any pronounced adsorption of the acid on the colloid had taken place, identical acid mixtures were similarly examined in absence of any colloid, *i.e.*, with 10 c.c. of water substituted in each case for the 10 c.c. of sol used previously.

Acid.	Conc. in milli-equivs. per litre.	p_H of medium after precipitation.	p_H of acids alone.
Hydrochloric	17·1	1·88	1·80
Sulphuric	26·0	1·80	1·73
Acetic	1800	2·27	2·17
Citric	642	1·91	1·83

The results show: 1. An agreement in p_H values, in the case of three of the acids, which is as good as has yet been attained by this method. Such discrepancy as exists the author believes to be due to the difficulty of deciding whether "complete precipitation" has taken place or not, which might be overcome by the use of some form of colorimeter.

2. That citric acid appears to behave normally, contrary to what was found by Bradfield.

3. That some adsorption, either of hydrogen ions or acid molecules, on the precipitating colloid has taken place (compare third and fourth columns).

4. That acetic acid precipitates at a p_H distinctly lower than that of the other acids. This may be due either to a specific adsorption of the anion, or to the action of the undissociated acid molecules present at such a relatively high concentration.

Effect of the Oxalic Anion.—In the usual preparation of Prussian blue sols the dye is peptised by a solution of oxalic acid. A strong specific adsorption of the oxalic ion is inferred. Consequently, precipitation of such sols by means of oxalic acid solutions would not be expected. The sol already studied was not affected at all by concentrations of oxalic acid up to 100 milli-equivs. per litre. With the object of investigating the effect of the oxalic ion, a Prussian blue sol was prepared without the aid of oxalic acid, and its precipitation carried out. The dye was prepared exactly as before, thoroughly washed, and a sol obtained by repeatedly grinding the solid with water and filtering. The sol was dilute,

but perfectly stable after standing for 3 weeks. Analysis showed it to contain 0·072 g. of solid per litre. The stock solutions were *N*-oxalic and 0·11*N*-hydrochloric acid, and the technique was the same as that described above. Precipitation by oxalic acid occurred at a high, but quite definite concentration, whereas only a very small amount of hydrochloric acid was required. The p_H of the precipitating medium was observed as before.

Acid.	Conc. in milli-equivs. per litre.	p_H of medium after precipitation.
Hydrochloric	1·1	2·63
Oxalic	303 to 404	0·91 to 0·79

In the case of oxalic acid, precipitation was partial at the lower, but complete at the higher, concentration. The critical concentration lies between these two values. At a concentration of 202 milli-equivs. of oxalic acid per litre the sol showed no signs of precipitation after several days.

In view of the peptising effect of this acid, already referred to, the possibility of its use as a precipitant is interesting. Once precipitated by this acid, the dye could not be peptised by shaking with the precipitating mixture, whereas precipitates produced by other acids were readily peptised by adding a solution of oxalic acid and shaking.

In the high concentration and p_H values which oxalic acid demands for flocculation of the dilute sol, a strong protective adsorption of the anion is indicated.

My thanks are due to Mr. A. E. Clarence Smith for his advice and assistance.

UNIVERSITY COLLEGE, SOUTHAMPTON. [*Received, July 25th,* 1925.]

CCCVI.—*The Constitution of the Thionic Acids.*

By ISRAEL VOGEL.

ALTHOUGH the problem of the constitution of the thionic acids has occupied the attention of many investigators (compare Fordos and Gelis, *Compt. rend.*, 1842, **15**, 920; Blomstrand, "Chemie der Jetztzeit," p. 157; Mendeléev, *Ber.*, 1870, **3**, 870; Michaelis, *Annalen*, 1873, **170**, 37; Spring, *Ber.*, 1874, **7**, 1161; Debus, J., 1888, **53**, 280; Hertlein, *Z. physikal. Chem.*, 1896, **19**, 286; Riesenfeld and Feld, *Z. anorg. Chem.*, 1921, **119**, 225; Martin and Metz, *ibid.*, 1923, **127**, 82; Benrath, *Z. angew. Chem.*, 1922, **35**, 33; Raschig, "Schwefel und Stickstoffstudien," 1924, p. 305; Vogel, *Chem. News*, 1924, **128**, 325, 343, 361; Vogel, Thesis, 1925, University of London; the last-named contains a complete review of

the literature), it cannot be said that a final or even a satisfactory solution has yet been attained.

In the course of an investigation of sulphur sesquioxide (Vogel and Partington, this vol., p. 1514) it became evident that none of the formulæ hitherto proposed could give a rational explanation of the experimental facts recorded therein. For example, the gradual increase with time of the relative quantities of tetra- and penta-thionates in the products obtained by the interaction of sulphur sesquioxide with water, with sodium ethoxide, and with the blue solution obtained by the dissolution of sulphur in 65% oleum, respectively, and also the almost exclusive formation of trithionate in the reaction between concentrated potassium acetate solution and a solution of sulphur sesquioxide in oleum, were some of the facts for which an explanation had to be found. In addition to these, the liberation of *two* atoms of sulphur from pentathionates by bromine and by mercuric cyanide (Debus, *loc. cit.*), and by mercuric chloride (Sander, *Z. angew. Chem.*, 1916, **29**, 11; compare Riesenfeld and Feld, *loc. cit.*), the separation of *one* atom of sulphur from pentathionates on treatment with cold sodium carbonate solution (Raschig, *op. cit.*, p. 273), the conversion of tetrathionates into pentathionates by acidified sodium thiosulphate solution and the formation of dithionates by the action of acid potassium permanganate solution on trithionates (Raschig, *op. cit.*), the strong acidity of the thionic acids and the non-formation of complex-ions with mercury or silver salts (Hertlein, *loc. cit.*), the difference in refractivity corresponding to bivalent sulphur between two consecutive thionates, *e.g.*, between $K_2S_4O_6$ and $K_2S_5O_6$, are some of the chief experimental facts the interpretation of which is not possible on any one set of formulæ.

The following formulæ, which are in agreement with experiment, are proposed for the thionic acids:

$\begin{matrix}SO_2\cdot OH\\SO_2\cdot OH\end{matrix}$	$S<\begin{matrix}SO_2\cdot OH\\SO_2\cdot OH\end{matrix}$	$S{:}S<\begin{matrix}SO_2\cdot OH\\SO_2\cdot OH\end{matrix}$	$S{:}S{:}S<\begin{matrix}SO_2\cdot OH\\SO_2\cdot OH\end{matrix}$
Dithionic acid.	Trithionic acid.	Tetrathionic acid.	Pentathionic acid.

It might be of interest, in view of the controversy as to the relative stabilities of the thionic acids (compare Riesenfeld and Feld, *loc. cit.*; Foerster and Hörnig, *Z. anorg. Chem.*, 1922, **125**, 86), to point out that according to the above formulæ the relative stabilities should decrease in the order di-, tri-, tetra-, and penta-thionic acid. This is in accord with the thermochemical measurements of Martin and Metz (*ibid.*, 1923, **127**, 83).

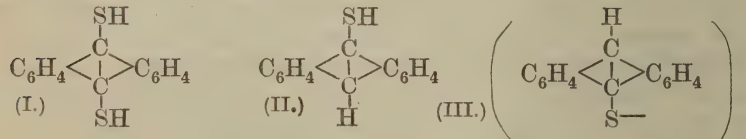
EAST LONDON COLLEGE,
UNIVERSITY OF LONDON.

[*Received, August 5th*, 1925.]

CCCVII.—meso-*Thioanthracene Derivatives. Part II. Dianthranyl Disulphide and Dianthranyl Tetrasulphide.*

By William Herbert Cooke, Isidor Morris Heilbron, and George Hugh Walker.

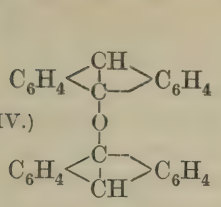
The action of the equivalent amount of sodium hydrosulphide (2 mols.) upon 9 : 10-dibromoanthracene in amyl-alcoholic solution has been shown (Heilbron and Heaton, J., 1923, **123**, 173) to give rise to a complex series of *meso*-thioanthracene derivatives, but the conditions attending the production of any particular compound were obscure, as successive precisely similar experiments did not invariably lead to the same substances. In continuing this investigation, the effect of employing a large excess of sodium hydrosulphide (4 mols.) was first studied, as it was hoped thus to be able to isolate the disodium salt of the hypothetical 9 : 10-dithiolanthracene (I), which, as previously stated, is to be regarded as the initial product. Actually, however, the reaction proceeded in a wholly different direction, the product containing 30—40% of dianthranyl disulphide (III) (Friedländer and Simon, *Ber.*, 1922, **55**, 3969).



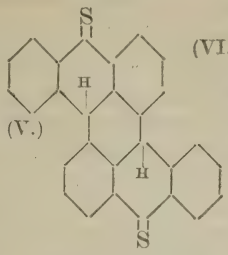
The presence of this compound in such large quantities harmonises well with the view that 9 : 10-dithiolanthracene truly represents the first stage in the reactions. Its formation is doubtless the result of reduction of the dithiolanthracene to 9-anthranyl mercaptan (II) during the course of the reaction, followed by oxidation of the latter substance to the disulphide during the working-up process (see experimental part). In addition to dianthranyl disulphide a compound containing neither sulphur nor halogen was isolated and to this the structure (IV) has been assigned on the grounds that on reduction it yields both anthranol and anthracene. It is probably formed from 9-anthranyl mercaptan by hydrolysis and is the oxygen analogue of the dianthranyl sulphide (*loc. cit.*).

The effect of employing less than one equivalent of sodium hydrosulphide was the production of a large quantity of dithioheptacyclene (V) (80—90% yield); which is invariably produced

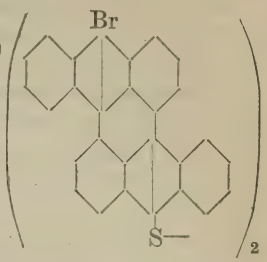
in 10% yield when equivalent quantities of sodium hydrosulphide and 9 : 10-dibromoanthracene are employed (*loc. cit.*).



(IV.)



(V.)



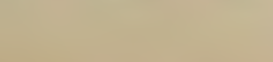
(VI.)

The effect of sodium sulphide, sodium disulphide, and sodium polysulphides upon dibromoanthracene has also been examined.

Sodium sulphide. When the equivalent quantity of this salt was used, the dibromoanthracene ceased to separate from the amyl-alcoholic solution after 3 days' continuous boiling; the products were unchanged material and small quantities of dianthranyl disulphide and anthracene. Even when a considerable excess of sodium sulphide was present, very little change was noted on simply boiling the reactants under reflux, but on heating in an autoclave for 2 hours at 150°, the dibromoanthracene was completely converted into dithioheptacyclene.

Sodium disulphide. On refluxing a solution of the reactants in amyl or butyl alcohol the dibromoanthracene rapidly disappeared; after 8 hours, the solution was deep red and addition of small quantities of water precipitated practically pure dianthranyl disulphide (average yield: 60%). When ethyl alcohol was used as solvent, dibromoanthracene was recovered even after 3 days' boiling. On the other hand, by heating the reactants with amyl alcohol in an autoclave for 4 hours at 200° a yellow, amorphous compound (insoluble in all media) was formed to which the constitution (VI) has been tentatively assigned. Its formation may be attributed to a fusion of the anthracene molecules with loss of hydrogen bromide in an analogous manner to that leading to dithioheptacyclene.

Sodium polysulphides. On treatment of 9 : 10-dibromoanthracene in boiling amyl-alcoholic solution with this mixture of salts, in which the tetrasulphide is probably the main constituent, a good yield was obtained of the substance to which Heilbron and Heaton (*loc. cit.*) had assigned the dithiodianthrone disulphide structure (VII) on the grounds that it was soluble in boiling alcoholic potash,

(VII.)  (VIII.)

supposedly existing in the solution as the potassium salt of the tautomeric dithiodianthranol derivative (VIII). Owing to the ease with which this substance can now be obtained, it has been possible to make a more detailed examination of its properties. The action of boiling alcoholic potash has been confirmed in so far as the substance dissolves completely on boiling, forming a blood-red solution. In no case, however, could the original compound be recovered, for on acidification by means either of dilute acetic acid or of carbon dioxide in ice-cold solution, hydrogen sulphide was evolved and dianthranyl disulphide produced. It is impossible to reconcile the ready formation of the disulphide in this way with the structure (VIII), and it would appear that the true constitution of this compound is that of an organic tetrasulphide the structure of which could be expressed by one or other of the following formulæ :

$C_{14}H_9{\cdot}S{\cdot}\underset{\|}{S}{\cdot}\underset{\|}{S}{\cdot}C_{14}H_9$ (IX.) $\quad$ $C_{14}H_9{\cdot}S{\cdot}\underset{\|}{S}{\cdot}S{\cdot}C_{14}H_9$ (X.) $\quad$ $C_{14}H_9{\cdot}S{\cdot}S{\cdot}S{\cdot}S{\cdot}C_{14}H_9$ (XI.)

Holmberg (*Annalen*, 1907, **359**, 81), in a critical review of the structure of organic tetrasulphides, comes to the conclusion that the straight-chain type is the most probable, and in the case of the compound under review, (XI) is wholly in keeping both with its method of formation and with its ease of decomposition. Again, an attempt to form a methiodide by boiling the dianthranyl tetrasulphide with methyl iodide failed, and this is in agreement with the results obtained by Smythe and Foster (J., 1910, **97**, 1197) in their work on benzyl tetrasulphide.

Experimental.

Treatment of 9 : 10-*Dibromoanthracene with Excess of Sodium Hydrosulphide.—Dianthranyl disulphide* (III). A solution of sodium amyloxide (sodium 9 g., amyl alcohol 1000 c.c.) was saturated with dry hydrogen sulphide with precautions against clogging. 9 : 10-Dibromoanthracene (30 g.) was then added and the mixture heated to boiling, the stream of hydrogen sulphide being maintained throughout the whole reaction. The solution became light red and then dark brown; after 12 hours, no 9 : 10-dibromoanthracene separated on cooling. No dithioheptacyclene was thrown out of solution, as was invariably the case when the equivalent quantity of sodium hydrosulphide was employed (Heilbron and Heaton, *loc. cit.*). The cold amyl-alcoholic solution was shaken with water to remove inorganic salts, and the brown precipitate thereby produced was removed, dried, and repeatedly crystallised from benzene, dianthranyl disulphide being obtained in orange prisms, m. p. 223°. On treatment with zinc dust and glacial acetic acid,

it was readily reduced to 9-anthranyl mercaptan, m. p. 90° (Friedländer and Simon, *loc. cit.*) (Found : C, 80·1; H, 4·3; S, 15·0. Calc., C, 80·4; H, 4·3; S, 15·3%). In later experiments, it was found that the yield of dianthranyl disulphide could be considerably increased (40% calculated on the dibromoanthracene) by cutting off the current of hydrogen sulphide during the heating process. Experiments were carried out substituting 9 : 10-dichloroanthracene for the bromo-derivative, potassium for sodium, and butyl alcohol for amyl alcohol, but with none of these variations was the yield of disulphide so satisfactory.

Dianthranyl oxide (IV). The amyl-alcoholic mother-liquors from the above experiment were dried over anhydrous sodium sulphate and concentrated; the yellow substance that slowly separated from the cold solution proved extremely troublesome to crystallise, but was ultimately obtained in long, straw-coloured needles from alcohol, m. p. 213° (Found : C, 90·6; H, 5·0. $C_{28}H_{18}O$ requires C, 90·8; H, 4·9%). Dianthranyl oxide was not affected by alkalis alone, but on reduction with zinc dust and hot sodium hydroxide solution it yielded anthracene (identified as the picrate) and anthranol, m. p. 120° (not sharp) (compare Meyer, *Annalen*, 1910, **379**, 37). Like so many of these derivatives, dianthranyl oxide was not invariably obtained in all the experiments carried out and it has been impossible to ascertain the exact conditions of formation.

Treatment of 9 : 10-*Dibromoanthracene with less than one Equivalent of Sodium Hydrosulphide.*—When less than 1 equivalent of sodium (2 g. Na : 20 g. dibromoanthracene) was used under the conditions described in the first experiment, dithioheptacyclene began to separate after 6 hours; the reaction was completed after 9 hours' boiling. The product was purified as described in Part I (yield 80—90%).

Action of Sodium Sulphide.—9 : 10-Dibromoanthracene (15 g.) was added to a solution (300 c.c.) of sodium sulphide (16 g.) prepared by mixing solutions of equivalent quantities of sodium hydrosulphide and sodium amyloxide in amyl alcohol. Very little change occurred on heating at 140°, and even after 2 days' boiling the bulk of the dibromoanthracene separated on cooling. The mixture was therefore heated in an autoclave at 150° for 2 hours. On cooling, dithioheptacyclene separated in almost quantitative yield (Found : C, 80·8; H, 3·9; S, 15·2. Calc., C, 80·8; H, 3·8; S, 15·4%). Using only the equivalent quantity of sodium sulphide had very little effect, a small quantity of dianthranyl disulphide, together with anthracene and unchanged dibromoanthracene, being obtained after 3 days' boiling.

Treatment of 9 : 10-*Dibromoanthracene with Sodium Disulphide.—Dianthranyl disulphide.* A solution of sodium amyloxide (300 c.c.) containing 6 g. of sodium was converted into sodium sulphide as described above, and the theoretical quantity of powdered sulphur (4 g.) added. The mixture was gently boiled for 3 hours together with dibromoanthracene (15 g.), the colour becoming light red and finally dark brown. The solution was filtered from a small residue of unchanged 9 : 10-dibromoanthracene, the filtrate distilled to remove as much amyl alcohol as possible, and then steam-distilled. The residual light red alkaline solution contained a deep brown semi-solid mass which quickly solidified. After six crystallisations from benzene in presence of animal charcoal, orange crystals (m. p. 223°) of dianthranyl disulphide were obtained (weight of crude product : 10 g.).

By employing butyl alcohol (b. p. 116°) in place of amyl alcohol and heating for 8 hours, the whole of the dibromoanthracene was utilised and a dark red solution resulted from which the dianthranyl disulphide was completely precipitated by treatment with small quantities of water. By adopting this method, resin formation was prevented and an average yield of 60% of dianthranyl disulphide, calculated on the weight of the dibromoanthracene used, resulted (Found : C, 80·3, 80·1; H, 4·5, 4·6; S, 15·0. Calc., C, 80·4; H, 4·3; S, 15·3%).

ms-*Dibromodiheptacyclene disulphide* (VI) was obtained by heating a mixture of 9 : 10-dibromoanthracene (15 g.), crystallised sodium disulphide (5 g.), and amyl alcohol (1000 c.c.) in the autoclave for 4 hours at 200°. The yellow, amorphous product was boiled with water to remove inorganic matter and again, after drying, with xylene to remove unchanged dibromoanthracene. It was insoluble in all organic solvents and resisted reduction and the action of boiling alcoholic potash (Found : C, 72·5; H, 3·5; S, 6·7; Br, 17·4. $C_{56}H_{28}Br_2S_2$ requires C, 72·7; H, 3·0; S, 6·9; Br, 17·4%).

Dianthranyl Tetrasulphide (XI).—A sodium polysulphide mixture was prepared by slowly heating hydrated sodium sulphide ($Na_2S,9H_2O$; 60 g.) with finely powdered rock sulphur (24 g. for 2 hours at a maximum temperature of 150°. The fused orange melt was cooled and while still syrupy was added to 9 : 10-dibromoanthracene (40 g.) dissolved in amyl alcohol (700 c.c.); after being heated under reflux for 2 days, the solution was deep red. On standing over-night or longer, dianthranyl tetrasulphide separated. After boiling with water to dissolve inorganic matter, it was crystallised from benzene, separating in yellow spangles, m. p. 190° (Heilbron and Heaton, *loc. cit.*, give m. p. 194°) (yield : 33%). If the amyl alcohol is impure or if the crude polysulphide is allowed to

solidify before addition to the amyl-alcoholic solution, a quantity of free sulphur is deposited with the dianthranyl tetrasulphide, rendering purification extremely difficult. The identity of this compound with Heaton and Heilbron's dithiodianthrone disulphide (VIII) was proved by mixed melting-point determinations and by analysis (Found: C, 69·9, 69·9; H, 4·2, 4·0; S, 26·2. Calc., C, 69·7; H, 3·7; S, 26·5%).

Dianthranyl tetrasulphide was boiled with alcoholic sodium hydroxide for 3 hours, and the hot, deep red solution filtered and set aside; dianthranyl disulphide was slowly deposited. A repeat experiment was carried out, but in this case the filtrate, which was immersed in powdered ice, was acidified with dilute acetic acid; hydrogen sulphide was evolved and a buff-coloured precipitate of dianthranyl disulphide separated. That the tetrasulphide is decomposed by the alkali to give in the first place 9-anthranyl mercaptan was proved by the actual isolation of this compound from the reaction mixture in which the heating was suspended immediately the dianthranyl tetrasulphide had gone into solution. The hot solution was rapidly saturated with carbon dioxide and the residue washed with hot water to remove sodium carbonate. After drying, it separated from light petroleum in yellow crystals, m. p. 90°, which were freely soluble in dilute aqueous sodium hydroxide and readily oxidised by potassium ferricyanide solution to the disulphide.

THE UNIVERSITY, LIVERPOOL. [*Received, July 18th*, 1925.]

CCCVIII.—*The Reaction between Sodium Hypobromite and Carbamide.*

By MAXWELL BRUCE DONALD.

THE reaction between carbamide and sodium hypobromite may be represented as:

$$CON_2H_4 + 3NaOBr \longrightarrow CO_2 + N_2 + 3NaBr + 2H_2O,$$

but in actual practice it is found that it never goes to completion. The course of the reaction can be followed by estimating (1) the amount of nitrogen evolved, (2) the amount of hypobromite decomposed, or (3) the amount of carbonate formed. All these methods give substantially the same results and indicate that, with the usual methods of performing the experiment, the reaction goes only to about 90% of completion.

The incompleteness of the reaction has been attributed to various

causes, such as (1) the solubility of nitrogen in the hypobromite solution, (2) the formation of a compound of carbamide and bromous acid (Hüfner, *J. pr. Chem.*, 1871, **3**, 1), (3) the impurity of the nitrogen (Rayleigh and Ramsay, *Phil. Trans.*, 1895, **186**, *A*, 187; Rayleigh, *Proc. Roy. Soc.*, 1898, **64**, 95; Krogh, *Z. physiol. Chem.*, 1913, **84**, 379; Hurtley, *Biochem. J.*, 1921, **15**, 11), (4) the formation of oxides of nitrogen in the solution (Fauconnier, *Bull. Soc. chim.*, 1880, **33**, 102; Luther, *Z. physiol. Chem.*, 1889, **13**, 500; Krogh, *loc. cit.*). None of these explanations, however, is adequate (see, for example, Lescœur, *J. Pharm. Chim.*, 1919, **20**, 305; Werner, J., 1922, **121**, 2318; Margosches and Rose, *Biochem. Z.*, 1923, **137**, 542).

The alternative suggestion (Fenton, J., 1878, **33**, 300; P., 1895, 138; see also Lescœur, *loc. cit.*; Margosches and Rose, *loc. cit.*) that the reaction does not go to completion because of the formation of sodium cyanate is supported by the evidence brought forward in the present communication. The work of Margosches and Rose, on which the view was based that the formation of sodium cyanate cannot be the chief cause of the nitrogen deficit, is inconclusive, since no account was taken of the composition of the hypobromite used.

Experimental.

The gasometric method was found to be unsatisfactory for two reasons. The usual solution (40% brominated 10*N*-sodium hydroxide)* was made by adding bromine to a sodium hydroxide solution cooled to below 0° and analysed for hypobromite by sodium arsenite and for total hypobromite and bromate by sodium thiosulphate. The original solution was then kept for 20 hours and analysed again. Although there was no change in the thiosulphate titration, the hypobromite had been half converted into bromate over-night. The old hypobromite solution evolved about 3% more nitrogen from a carbamide solution than the freshly prepared hypobromite. This, as will be seen from subsequent results, is probably due to the decreased ratio of hypobromite to hydroxide.

The other objection to this method is that the reaction between carbamide and hypobromite gives off a considerable amount of heat; in fact, Smith (*Chem. News*, 1895, **71**, 259) used such heat as a basis for determining the amount of carbamide in urine. Wagner (*Z. anal. Chem.*, 1874, **13**, 383) suggests keeping the reaction vessel under water; but the volume of gas only becomes constant 15

* A hypobromite solution made by adding 25 c.c. of bromine (1 equiv.) to 100 g. of sodium hydroxide (2·5 equivs.) dissolved in water, and making up to 250 c.c. is described as a 40% brominated 10*N*-sodium hydroxide solution.

minutes after the reaction, even when it is kept in a well-stirred thermostat. The factor generally given in text-books for 40% brominated 10*N*-sodium hydroxide is 0·92. Careful measurements with thermostat control, using freshly prepared cool hypobromite and applying all corrections to the volume of gas evolved, gave 0·90, whereas the titration method shows that the factor should be 0·87.

More trustworthy results were obtained by estimating the hypobromite decomposed. The procedure was to add the carbamide solution slowly to the hypobromite, allow the reaction to proceed with occasional shaking for 5 minutes, dilute the reaction mixture to 500 c.c., and add about 20 c.c. of 3*N*-hydrochloric acid and a solution containing about 5 g. of potassium iodide. The solution was kept for 2 minutes and then titrated with thiosulphate, with starch as an indicator. There was a certain tendency to " reblue " on standing. The difference between the amounts of thiosulphate required for this titration and for the hypobromite alone gives the equivalent amount of hypobromite which has been used up in the reaction. The carbamide was recrystallised three times from alcohol and dried at 100°.

A number of experiments were undertaken to determine the chief factors which influenced this reaction at room temperature. Excess of hypobromite had no effect, confirming previous observations on a similar reaction with ammonia (*Analyst*, 1924, **49**, 375). The actual concentration of the hypobromite had no effect at moderate concentrations. Thus a 40% brominated 4*N*-sodium hydroxide solution was diluted in steps down to 0·25*N* without any effect on the reaction. In stronger solutions of hypobromite, there are secondary effects due to time changes in the hypobromite–hydroxide ratio to be allowed for. The chief factor at room temperature was the extent to which the sodium hydroxide had been brominated.

Some of the experimental results obtained with carbamide and various hypobromite solutions are in Table I. The expression " c.c. thio. required " indicates the difference in thiosulphate required for a blank and that required after the carbamide has been added to the hypobromite.

Similar results are obtained with hypobromite solutions prepared from sodium hydroxide as strong as 2*N*. Both titration and gasometric methods show that the nitrogen deficit becomes greater as the percentage bromination increases until the hydroxide is 75% brominated. At this point a sudden change occurs, the amount of gas evolved still decreases, but a slow oxidation sets in. After 30 minutes, an amount of hypobromite is used up which is about equivalent to the

TABLE I.

Sodium thiosulphate 0·1963*N*. Sodium hydroxide 0·496*N*. 5 C.c. of carbamide solution contain 0·075 g., which is equivalent to 38·3 c.c. of thiosulphate.

No. of sol.	% Brominated.	C.c. of thio. required after 5 mins.	15 mins.	30 mins.	Carbamide decomposed %.
1	15	34·2	—	—	89·3
2	30	33·8	—	—	88·4
3	45	33·1	—	—	86·4
4	60	31·0	31·1	30·9	81·0
5	75	29·7	29·1	29·4	77·6
6	80	29·2	37·5	38·7	
7	85	33·5	38·6	37·8	
8	90	35·1	37·7	38·7	
9	95	36·5	37·9	38·5	
10	97·5	—	4·2	4·0	

quantity of carbamide taken (*i.e.*, 38·3 c.c. of thio.). When the sodium hydroxide is completely brominated, there is no gas evolution and no hypobromite is used up.

Sodium cyanate was prepared by the method of Leuchs and Geserick (*Ber.*, 1908, **41**, 4171) from urethane and sodium in boiling benzene and was twice recrystallised from pure alcohol. With it and with the same hypobromite solutions as before, the following results were obtained.

TABLE II.

5 C.c. of sodium cyanate taken contain 0·075 g., equiv. to 17·7 c.c. of 0·196*N*-thio.

No. of solution.	% Bromination.	C.c. of thio. after 5 mins.	15 mins.
5	75	—	—
6	80	0·4	0·3
7	85	0·4	0·3
8	90	1·0	0·7
9	95	17·9	18·0

There is no action of hypobromite on sodium cyanate below the composition 75% brominated. Above this value the hypobromite reacts slowly with the sodium cyanate, but with 100% brominated solutions there is a vigorous gas evolution from the mixture.

The figures for sodium cyanate (Nos. 7 and 8) do not show complete oxidation, as would be expected from the figures in Table I. Another series of experiments was therefore made with the same hypobromite solutions, using a mixture of carbamide and sodium cyanate.

These figures point to the fact that the deficit of nitrogen is due to the formation of sodium cyanate and that with hypobromite solutions brominated to more than 75% and less than 95% a secondary oxidation of the sodium cyanate is induced only if carbamide is present. They also show that the rate of this secondary oxidation

TABLE III.

5 C.c. of the solution contain 0·0375 g. each of carbamide and sodium cyanate, which are equivalent to 19·15 and 17·7 c.c. of 0·196*N*-thiosulphate respectively.

No. of solution.	% Bromination.	C.c. of thio. required after 5 mins.	15 mins.
4	60	16·2	16·1 carbamide alone
7	85	15·8	28·5
8	90	28·2	28·4

is greater with increase in the amount of bromination of the sodium hydroxide. Carbamide is not acted upon by 100% sodium hypobromite, as there is no excess of sodium hydroxide to decompose the compound which it probably forms with the bromine.

The potential of a platinum electrode dipping into the various solutions shows that there is no marked change in the oxidising power except in the neighbourhood of completely brominated solutions.

TABLE IV.

No. of solution.....	1	3	5	7	9	10
E.M.F. volt	+0·756	0·790	0·810	0·830	0·850	0·981

Summary.

The chief factor influencing the deficit of nitrogen in the reaction between carbamide and sodium hypobromite at room temperature is the extent to which the sodium hydroxide has been brominated. The effect of this variable has been studied for all brominations from 0 to 100%. The reaction does not go to completion owing to the formation of sodium cyanate. The amount of sodium cyanate formed becomes greater as the ratio of hypobromite to hydroxide increases until it corresponds to 75% bromination, when it is oxidised in a secondary reaction. Sodium cyanate solutions are not appreciably oxidised by 75 to 90% hypobromite solutions except in the presence of carbamide. With pure hypobromite (*i.e.*, without any excess of sodium hydroxide present) sodium cyanate solutions are vigorously decomposed. The experiments of Margosches and Rose proving that sodium cyanate is not formed in the reaction are inconclusive, since they do not take into account the effect of the composition of the hypobromite. The use of 10*N*-sodium hydroxide solutions for the estimation of carbamide gasometrically leads to inaccurate results.

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, May 16th,* 1925.]

CCCIX.—*Nitrosation of Phenols. Part II. Nitrosation of* 3-*Bromo-*, 2-*Bromo-*, 3-*Iodo-*, *and* 2-*Iodo-phenol. Evidence for the Nitroso-formula of* 4-*Nitrosophenol.*

By Herbert Henry Hodgson and Francis Harry Moore.

The investigation now to be described, dealing mainly with the nitrosation of 3-bromo- and 3-iodo-phenol, supplements work on 3-chlorophenol (J., 1923, **123**, 2499).

Unlike 3-chloro-4-nitrosophenol, 3-bromo-4-nitrosophenol is so sensitive to transformation that the quinoneoxime form is produced in every solvent except ether. 3-Iodo-4-nitrosophenol has been obtained only in the quinoneoxime modifications. Geometrical isomerides of both compounds have been isolated which exhibit differences in colour (see also Kehrmann and Wolff, *Ber.*, 1900, **33**, 1539; Kehrmann and Denk, *ibid.*, p. 3297). Oxidation to the corresponding halogenated nitrophenols has established the 4-positions of the nitroso-groups, and molecular-weight determinations the unimolecular character of the isomerides.

2-Chloro- and 2-bromo-4-nitrosophenol were readily obtained by the general process for nitrosating *m*-halogenated phenols (*loc. cit.*); but from 2-iodophenol a tar was produced, and the nitroso-compound was obtained only by working at great dilution and in the presence of acetic instead of sulphuric acid. These three nitroso-compounds could not be converted into the quinoneoxime forms, the immobility of the phenolic hydrogen in proximity to a halogen atom being thus made manifest.

A very fine specimen of nitrosophenol free from resinous matter has been prepared from phenol by the general nitrosation method; it melts at 133°, *i.e.*, 7° higher than the m. p. (126°) usually recorded. A specimen prepared 2 years ago is still in good condition.

The data in the following table are claimed to support the view that 4-nitrosophenol is a genuine nitroso-compound and not a quinoneoxime.

Substance.	M. p. of nitroso-compound.	M. p. of quinoneoximes.
Phenol	133° (126° recorded)	126° (prepared from benzoquinone)
2-Chlorophenol	148° with decomp.	—
2-Bromophenol	150° „ „	—
2-Iodophenol	Decomp. 152°	—
3-Chlorophenol	135° with decomp.	172° and 178°
3-Bromophenol	139° „ „	189° and 190°
3-Iodophenol	—	Decomp. 185—195°
2:5-Dichlorophenol	146°	Decomp. 155—160°
ψ-Cuminol *	134° (4-nitroso-2:3:5-trimethylphenol)	184°

* Nietzki and Schneider, *Ber.*, 1894, **27**, 1426.

Experimental.

Nitrosation of 3-Bromo-, 2-Bromo-, and 3-Iodo-phenol.—The method for preparing 3-chloro-4-nitrosophenol (J., 1923, **123**, 2502) was found generally applicable; the nitroso-compounds, however, formed gradually and separated, partly as pale yellow crystals (0·5—1 g.) and partly as tars, from which, after draining and washing with cold benzene, about 2 g. more of the products were obtained.

3-Bromo-4-nitrosophenol dissolves readily in alcohol or ether and is moderately easily soluble in hot benzene or light petroleum, but almost insoluble in the cold solvent. It was obtained in yellow needles, m. p. 139° (decomp.), by addition of light petroleum to an ethereal solution (Found: Br, 39·5; N, 7·0. $C_6H_4O_2NBr$ requires Br, 39·6; N, 6·9%).

*3-Bromo-*p*-benzoquinone-4-oxime* was obtained in red needles when the preceding compound was crystallised from benzene, dilute hydrochloric acid, and dilute alcohol; the three products melted and decomposed at 187°, 188°, and 186°. On recrystallisation from dilute hydrochloric acid, the quinoneoxime was obtained in orange needles, m. p. 188° (decomp.) (Found: Br, 39·6; N, 7·1; *M*, cryoscopic in phenol, 189. $C_6H_4O_2NBr$ requires Br, 39·6; N, 6·9%; *M*, 202). All the solvents tried except cold ether effected the conversion.

Action of Alkalis on 3-Bromo-4-nitrosophenol.—The nitroso-compound dissolves in aqueous sodium hydroxide (10%) to a red solution which froths after a few seconds. If the solution is acidified immediately, a pale yellow almost colourless substance of m. p. 189—190° (needles from benzene) is precipitated (Found: Br, 39·55; N, 7·2), but if it is kept for some time a dark-coloured substance of indefinite m. p. is produced on acidification. Sodium carbonate effects the same transformation unaccompanied by frothing, or decomposition on short standing.

Interconversion of the Geometrical Isomerides.—Dissolution of the orange form of the quinoneoxime in alkalis (unaccompanied by frothing), followed by acidification in the cold, produces the colourless form, and crystallisation of the latter from dilute hydrochloric acid converts it into the orange isomeride.

Liebermann's Nitroso-reaction.—All three products gave identical results owing to the ready conversion of two of them into the acid-stable form. To 0·05 g. of each isomeride, 0·1 g. of phenol and 1 c.c. of concentrated sulphuric acid were added. The solutions were deep green and became brownish-red on dilution and then violet on addition of sodium hydroxide.

Oxidation of 3-Bromo-4-nitrosophenol and its Tautomerides to 3-Bromo-4-nitrophenol.—Oxidation proceeds much more readily than in the case of 3-chloro-4-nitrosophenol. A solution of 0·5 g. of any one of the three isomerides in water (100 c.c.) containing potassium ferricyanide (5 g.) and sodium hydroxide (5 g.) was kept for 48 hours at room temperature and then acidified with dilute sulphuric acid (25%). The solution was filtered, shaken with ether, the solvent removed from the extract, the residue treated with a minimum of aqueous sodium hydroxide (10%), and the alkaline solution acidified in the cold with concentrated hydrochloric acid; the brown precipitate thus obtained crystallised from benzene in almost colourless needles, m. p. 131° (Auwers and Deines, *loc. cit.*, give m. p. 130—131°) (Found : Br, 36·75; N, 6·5. Calc. for $C_6H_4O_3NBr$, Br, 36·7; N, 6·4%).

2-*Bromo-4-nitrosophenol.*—This nitroso-compound is not transformed into a quinoneoxime by hot dilute mineral acids. It crystallises from benzene in light brown needles and from dilute alcohol in red needles, m. p. 150° (Found : Br, 39·4; N, 7·0. $C_6H_4O_2NBr$ requires Br, 39·6; N, 6·9%). The colour produced in the Liebermann nitroso-reaction is deep green and changes to wine-red on dilution; it reverts to deep green in aqueous sodium hydroxide. Oxidation with ferricyanide as described above converts the nitroso-compound into 2-bromo-4-nitrophenol, m. p. 112° (Found : Br, 36·6; N, 6·5. Calc., Br, 36·7; N, 6·4%).

3-*Iodo*-p-*benzoquinone*-4-*oxime.*—The nitrosation product of 3-iodophenol has no m. p.; it darkens at 170—180°, begins to decompose at 185°, and a deep reddish-brown vapour is evolved at 200°. The compound is readily soluble in alcohol or ether, moderately easily soluble in hot benzene but very sparingly soluble in the cold solvent, and insoluble in light petroleum. The yellow needles obtained from its solution in benzene or hot dilute hydrochloric acid decompose at 185—195°; if the latter solution is boiled for a few minutes, iodine is liberated and no crystallisation ensues. Light petroleum added to an ethereal solution of the quinoneoxime produces small, deep yellow prisms. This isomeride, which is tentatively assumed to be the *syn*-form (compare J., 1923, **123**, 2499), has a normal molecular weight in phenol solution (Found : N, 5·8; I, 50·9; *M*, cryoscopic in phenol, 254. $C_6H_4O_2NI$ requires N, 5·6; I, 51·0%; *M*, 249).

The *syn*-modification dissolves in 10% aqueous sodium hydroxide without frothing. From the red solution, on acidification, a very pale straw-coloured substance is precipitated. This, the *anti*-form, decomposes at about 185° and is highly dissociated in phenol solution (Found : N, 5·7; I, 50·9%; *M*, cryoscopic in phenol, 160).

The Liebermann reaction produced a yellowish-brown colour, which changed to reddish-brown when the solution was diluted or made alkaline. Decomposition appears to have taken place.

Oxidation with alkaline ferricyanide as described above gave *3-iodo-4-nitrophenol*, which crystallised from alcohol in long, slender, almost colourless needles, m. p. 123° (Found: N, 5·5. $C_6H_4O_3NI$ requires N, 5·3%), and was identified by comparison with a specimen prepared by nitrating 3-iodophenol.

Preparation of 2-Iodophenol.—2-Iodonitrobenzene was obtained in 91% yield from *o*-nitroaniline by the usual procedure; only a slight excess of potassium iodide, however, was employed. It melted at 50—51° (Nölting and Wrzesinski, *Ber.*, 1875, **8**, 820, give m. p. 43°). Its reduction with tin and hydrochloric acid produced a mixture of 2-iodo- and 2-chloro-aniline, and the yield of the former obtained by means of ferrous sulphate and ammonia was poor (compare Körner and Wender, *Gazzetta*, 1887, **17**, 486). 2-Iodonitrobenzene (28 g.), iron filings (28 g.), glacial acetic acid (70 c.c.), and water (70 c.c.) were mixed together and the mild reaction was completed by heating on the water-bath. The product was made alkaline with sodium bicarbonate and distilled with steam. The 2-iodoaniline thus obtained (22 g. or 89·5%; m. p. 57°. Körner and Wender, *loc. cit.*, give m. p. 56·5°) was converted, by rapidly cooling a hot solution in concentrated sulphuric acid (20 c.c.) and water (50 c.c.), into small crystals of the sulphate, which was diazotised and the excess of nitrous acid destroyed by carbamide; the diazo-solution was added drop by drop to a boiling solution of sulphuric acid (50 c.c.) and water (50 c.c.) through which a current of steam was passing. The 2-iodophenol thus obtained (yield 20 g. or 91%) melted at 40° after crystallisation from ether (Schall, *Ber.*, 1883, **16**, 1897; 1887, **20**, 3363, gives m. p. 39—40°).

Nitrosation of 2-Iodophenol.—The general method was useless in this case, tarry matter only being formed. The main product of the action of amyl nitrite and glacial acetic acid on 2-iodophenol in benzene solution was 2-iodo-6-nitrophenol, which was isolated by means of its volatility in steam. This compound, which was also prepared by nitrating 2-iodophenol, crystallised from light petroleum in bright yellow, feathery needles, m. p. 109°, and formed a red sodium salt.

A solution of 2-iodophenol (4 g.) and sodium nitrite (7 g.) in water (850 c.c.) was cooled to 10° and treated gradually with a mixture of glacial acetic acid (4·5 c.c.) and water (5 c.c.). After 24 hours, the solution was filtered, and shaken with ether. The extract was treated with 10% sodium hydroxide, and the deep-

coloured aqueous layer very cautiously acidified in the cold. The yellow precipitate (1 g.) of 2-*iodo*-4-*nitrosophenol* crystallised from benzene or dilute hydrochloric acid in yellow needles, which decomposed at 152°. No conversion into a quinoneoxime could be effected (Found: N, 5·7; I, 50·85; *M*, cryoscopic in phenol, 255. $C_6H_4O_2NI$ requires N, 5·6; I, 51·0%; *M*, 249). The colour produced in the Liebermann reaction was deep green; it changed to crimson on dilution and to blue when the solution was made alkaline. 2-Iodo-4-nitrophenol, m. p. 86—87°, was obtained by oxidising 2-iodo-4-nitrosophenol with ferricyanide and by nitrating 2-iodophenol (Found: N, 5·4. Calc., N, 5·3%).

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THE TECHNICAL COLLEGE,
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CCCX.—*Nitration of Phthal- and Succin-*p*-tolil.*

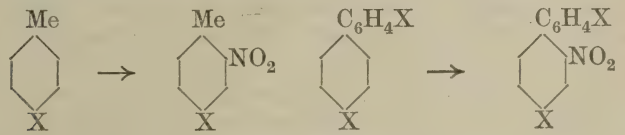
By OSCAR L. BRADY, WILLIAM G. E. QUICK, and WALTER F. WELLING.

THE nitration of aniline in the presence of a large quantity of concentrated sulphuric acid has long been known to give *m*-nitroaniline (Hübner and Frericks, *Annalen*, 1881, **208**, 299; Noelting and Collin, *Ber.*, 1884, **17**, 261; Bruns, *Ber.*, 1895, **28**, 1954; Tingle and Blanck, *Amer. Chem. J.*, 1906, **36**, 605), and of *p*-toluidine to give 2-nitro-*p*-toluidine. Acylated amines, however, on nitration usually give compounds in which the nitro-group has entered in the *o*- or *p*-position to the acylamino-group, but in some cases, if a large quantity of concentrated sulphuric acid is present, meta-substitution occurs; for example, under these conditions Noelting and Collin (*loc. cit.*) obtained after hydrolysis a small quantity of *m*-nitroaniline from acetanilide and a considerable quantity of 2-nitro-*p*-toluidine from aceto-*p*-toluidide; with plain nitric acid, however, the group entered in the ortho- or para-position to the acylamino-group. Phthal-*p*-tolil on nitration with a mixture of sulphuric and nitric acids gives mainly 2-nitro-*p*-toluidine (D.R.-P. 141893).

Sulphuric acid was employed in all these nitrations, but Miolati and Lotti (*Gazzetta*, 1897, **27**, i, 298) obtained 2-nitro-*p*-toluidine by nitrating succin-*p*-tolil with fuming nitric acid. (Compare also Cain and Micklethwait, *J. Chem. Soc.*, 1914, **105**, 1442, for the nitration of diphthalyltolidide.) This problem has now been investigated on more quantitative lines, the succinyl-, phthalyl-,

3-nitrophthalyl-, and tetrachlorophthalyl-compounds being nitrated with fuming nitric acid alone. Under these conditions, the aniline derivatives gave almost exclusively *p*-nitroaniline, but the derivatives of *p*-toluidine all gave 2-nitro-*p*-toluidine as the main product. It appears, therefore, that the dibasic acyl group does not sufficiently influence the amino-group to enable meta-substitution to occur, but so reduces its directive influence in the case of *p*-toluidine as to enable the comparatively feebly directive methyl group to take control. Nitrophthal-, tetrachlorophthal-, and succin-*p*-tolil gave approximately 84%, and phthal-*p*-tolil 76%, of 2-nitro-*p*-toluidine; the nature of the dibasic acid accordingly does not greatly influence the proportion of the isomerides formed.

This investigation arose from the study of the isomerism of the dinitrobenzidines (compare Brady and McHugh, J., 1923, **123**, 2047, where the literature of these compounds is summarised) and the behaviour of phthal-*p*-tolil in giving 2-nitro-*p*-toluidine with fuming nitric acid is consistent with the possibility that one of the nitro-groups in Bandrowski's dinitrobenzidine, obtained by the nitration of phthalylbenzidine, is in the meta-position to the amino-group, since one phthalylaminophenyl group can be regarded as replacing methyl in phthal-*p*-tolil.



$$X = \cdot N\!<\!\begin{matrix}CO\\CO\end{matrix}\!>\!C_6H_4.$$

Experimental.

The System 2-*Nitro*-p-*toluidine*–3-*Nitro*-p-*toluidine*.—The fusion diagram was constructed in the usual way from cooling curves of mixtures of the pure compounds. The results are in Table I. In the neighbourhood of the eutectic, crystallisation was very slow and the freezing point was easily missed if the rate of cooling exceeded 0·3° per minute; indeed with two mixtures no definite arrest was obtained until the eutectic temperature was reached, the freezing point being indicated only by the change of slope of the cooling curve; these values are given in brackets.

Nitration of Phthal-p-*tolil*.—Two parts of *p*-toluidine were heated with one of phthalic anhydride for 2 hours on the water-bath. The product was extracted repeatedly with hot alcohol, and the sparingly soluble residue crystallised from benzene. The phthalyl compound so obtained was added in small portions to 10 times its

TABLE I.

% 3-Nitro-*p*-toluidine.	F. p.	% 3-Nitro-*p*-toluidine.	F. p.	Eutectic.
0	74·8°	33·1	(60·9°)	56·1°
10·5	69·0	38·7	(65·6)	56·2
18·0	64·1	49·7	74·0	
23·5	60·3	55·0	78·4	
29·0	56·3	100	116·7	

weight of nitric acid (*d* 1·5) cooled in ice, the mixture kept on ice for 10 minutes and then poured on to crushed ice. When the ice had melted, the solid was collected, washed free from nitric acid, and hydrolysed by boiling with 2*N*-sodium hydroxide for 2 hours. After cooling, the mixture of nitrotoluidines which separated was collected, washed with water, and dried thoroughly in a vacuum over concentrated sulphuric acid. The freezing point was 59·9°, corresponding to 76% or 67% of 2-nitro-*p*-toluidine; the former value was shown to be correct by obtaining the right rise in freezing point by the addition of a known amount of pure 2-nitro-*p*-toluidine. The eutectic of the nitration mixture separated at 55·1° as against 56·2° for the synthetic mixture, indicating the presence of a small quantity of one or more other compounds, possibly 2 : 3-, 2 : 5-, 2 : 6-, and 3 : 5-dinitro-*p*-toluidines, all of which might be formed in the nitration; the amount, however, must be small and cannot greatly influence the relative proportions of the 2- and 3-nitro-*p*-toluidines here given. The separation of the main constituents of the hydrolysis product was achieved by acetylating with acetic anhydride with the addition of a drop of concentrated sulphuric acid, pouring into water, and crystallising the product three times from 50% alcohol, when pure 2-nitroaceto-*p*-toluidide was obtained. The mother-liquors from the crystallisation were hydrolysed by boiling with 2*N*-sodium hydroxide, and the amine was crystallised three times from 50% alcohol, when a small quantity of pure 3-nitro-*p*-toluidine was obtained. The crude phthalyl compound on crystallisation from benzene yielded pure phthal-2-nitro-*p*-tolil (D.R.-P. 141893).

Nitration of Succin-p-*tolil.*—Succin-*p*-tolil, prepared in an analogous way to the phthalyl derivative by means of succinic anhydride and heating to 150°, was nitrated in a manner similar to the above. The yield of mixed amines was poor; the product froze at 65·2°, corresponding to 84% of 2-nitro-*p*-toluidine.

Phthal-2-nitro-p-*toluidic and Succin-2-nitro*-p-*toluidic Acids.*—When phthal-2-nitro-*p*-tolil was warmed with 2*N*-sodium hydroxide, it dissolved completely; hydrochloric acid then precipitated the toluidic acid. This was purified by dissolving in cold dilute ammonia,

filtering off any amine, reprecipitating with hydrochloric acid, and crystallising from dilute alcohol, when *phthal*-2-*nitro*-p-*toluidic acid* was obtained as a cream-coloured, crystalline powder melting and decomposing indefinitely at about 160° (Found : N, 9·4. $C_{15}H_{12}O_5N_2$ requires N, 9·3%). The succintoluidic acid underwent further hydrolysis with ease, and in its preparation in an analogous manner to the above the alkali must not be warmed above 50° and solution must be obtained as rapidly as possible by vigorous shaking. After purifying by solution in ammonia and reprecipitation, it was dried and crystallised from benzene to which a few drops of alcohol had been added. *Succin*-2-*nitro*-p-*toluidic acid* crystallises in almost colourless, feathery needles, m. p. 163° (Found : N, 11·3. $C_{11}H_{12}O_5N_2$ requires N, 11·1%).

Nitration of 3-*Nitrophthal*-p-*tolil*.—A mixture of *p*-toluidine (30 g.) and nitrophthalic anhydride (25 g.) was heated for an hour at 130° with stirring. After cooling, the mass was dissolved in acetone, reprecipitated by the cautious addition of water, and the product crystallised from alcohol, when 3-*nitrophthal*-p-*tolil* was obtained as a yellow powder, m. p. 149° (Found : N, 9·8. $C_{15}H_{10}O_4N_2$ requires N, 9·9%). This was nitrated and hydrolysed as above, and the amines were extracted from the alkaline solution with ether. After drying in a vacuum, they froze at 64·7° (a repetition of the whole of the operations gave 64·5°), corresponding to 83·5% of 2-nitro-*p*-toluidine. The eutectic froze at 54·8°. The yield of amine from the nitrated product was small owing apparently to partial decomposition by the alkali, but other agents such as concentrated hydrochloric acid or 50% sulphuric acid did not bring about hydrolysis.

Nitration of Tetrachlorophthal-p-*tolil*.—Tetrachlorophthal-*p*-tolil prepared in a similar way to the nitrophthalyl compound consists of a pale yellow, crystalline powder, m. p. 145° (Found : Cl, 37·4. $C_{15}H_7O_2NCl_4$ requires Cl, 37·8%). Nitration and hydrolysis were carried out as with the nitrophthalyl compound, the yield of amines being small. The freezing point of the product was 65·1°, corresponding to 84·5% of 2-nitro-*p*-toluidine.

Nitration of Succinanil and Phthalanil.—These compounds were nitrated under identical conditions with the above. From the hydrolysed product pure *p*-nitroaniline was obtained by one crystallisation; the mother-liquor from this crystallisation was investigated, but no *m*-nitroaniline could be obtained by fractional crystallisation of the amine or of its acetyl derivative.

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CCCXI.—*Substitution in Vicinal Trisubstituted Benzene Derivatives. Part III.*

By Leon Rubenstein.

The mixture of 5- and 6-nitro-3-methoxy-2-ethoxybenzaldehydes produced by nitrating 3-methoxy-2-ethoxybenzaldehyde (Davies and Rubenstein, J., 1923, **123**, 2839) has now been separated into its constituents by the method employed by Perkin, Robinson, and Stoyle to separate the isomerides formed in the nitration of *o*-veratraldehyde (J., 1924, **125**, 2355); it contains 60% of the 5-nitro- and 40% of the 6-nitro-compound.

The same method was applied in an attempt to separate the mixture of 5- and 6-nitro-2 : 3-diethoxybenzaldehydes obtained in the nitration of 2 : 3-diethoxybenzaldehyde (Davies and Rubenstein, *loc. cit.*); these were condensed with *p*-toluidine and with *m*-nitroaniline, but in neither case could a complete separation of the Schiff bases be effected by fractional crystallisation.

Evidence was obtained, however, that both in the nitration of 3-methoxy-2-ethoxybenzaldehyde and of 2 : 3-diethoxybenzaldehyde the 4-nitro-aldehyde is formed in small quantity.

Experimental.

Nitration of 3-Methoxy-2-ethoxybenzaldehyde and Separation of the Products.—The following modified method of nitration (compare *loc. cit.*) renders the subsequent separation easier: 3-Methoxy-2-ethoxybenzaldehyde (12 g.) cooled to 0° is added drop by drop with vigorous stirring to nitric acid (30 c.c.; *d* 1·42), the temperature being maintained at 0°. The crystals of 5-nitro-3-methoxy-2-ethoxybenzaldehyde (7·4 g.) that separate after several hours are removed. The filtrate, on dilution with water, deposits a yellowish-white mixture of 5- and 6-nitro-3-methoxy-2-ethoxybenzaldehydes, which is collected and dried. This mixture (7·4 g.) is heated with *p*-toluidine (3·6 g.) on the steam-bath during 30 minutes, and alcohol is added until a boiling solution is obtained. 5-Nitro-3-methoxy-2-ethoxybenzylidene-*p*-toluidine separates on cooling, and the 6-nitro-isomeride from the filtrate after concentration. These substances can be almost completely separated by careful fractional crystallisation from alcohol.

5-*Nitro*-3-*methoxy*-2-*ethoxybenzylidene*-p-*toluidine* crystallises in pale yellow, slender needles, m. p. 148° (Found: N, 9·1. $C_{17}H_{18}O_4N_2$ requires N, 8·9%). It is readily hydrolysed by hot dilute hydrochloric acid, giving 5-nitro-3-methoxy-2-ethoxybenzaldehyde, m. p. 137°. 6-*Nitro*-3-*methoxy*-2-*ethoxybenzylidene*-p-*toluidine* crystallises in golden prisms, m. p. 88° (Found: N, 9·0%).

6-*Nitro*-3-*methoxy*-2-*ethoxybenzaldehyde*, readily obtained by hydrolysing the pure *p*-toluidine derivative with hot dilute hydrochloric acid, crystallises from aqueous alcohol in colourless, slender prisms, m. p. 57° (Found : N, 6·4. $C_{10}H_{11}O_6N$ requires N, 6·2%); the p-*nitrophenylhydrazone* consists of stout, brown needles, m. p. 188—189°. Treatment with acetone and alkali gives an indigotin derivative.

6-*Nitro*-3-*methoxy*-2-*ethoxybenzoic Acid.*—A mixture of the aldehyde (1 g.), water (10 c.c.), and potassium bicarbonate (0·6 g.) is boiled during the addition of hot 10% potassium permanganate solution (10 c.c.). The filtered, cooled solution is separated from a little unchanged aldehyde and acidified with hydrochloric acid. The 6-*nitro*-3-*methoxy*-2-*ethoxybenzoic acid* thus precipitated melts at 119—120° after crystallisation from hot water, in which it is fairly soluble (yield 50%) (Equiv., 240. $C_{10}H_{11}O_6N$ requires equiv., 241).

Nitration of 2 : 3-*Diethoxybenzaldehyde*.—This was carried out similarly to the nitration of 3-methoxy-2-ethoxybenzaldehyde. The material obtained (5·7 g.) was treated with *p*-toluidine (2·5 g.), and the product with alcohol, as described above ; 5-*nitro*-2 : 3-*diethoxybenzylidene*-p-*toluidine* (2·4 g.) crystallised in long, slender, cream needles, m. p. 105—106° (Found : N, 8·6. $C_{18}H_{20}O_4N_2$ requires N, 8·5%); further fractionation yielded a small quantity of a substance, m. p. 100° (Found : N, 8·7%).

5-*Nitro*-2 : 3-*diethoxybenzaldehyde*, which is readily obtained by hydrolysing the pure *p*-toluidine derivative, m. p. 105—106°, with hot dilute hydrochloric acid and recrystallising the product from aqueous alcohol, consists of white needles, m. p. 71°. It does not yield an indigotin derivative with acetone and alkali and gives no depression of m. p. when mixed with a sample of 5-nitro-2 : 3-diethoxybenzaldehyde obtained by nitrating 2-hydroxy-3-ethoxybenzaldehyde and methylating the product.

6-*Nitro*-2 : 3-*diethoxybenzaldehyde*, similarly obtained from the compound, m. p. 100°, crystallises from dilute alcohol in almost colourless needles, m. p. 75—76° (Found : N, 6·0. $C_{11}H_{13}O_5N$ requires N, 5·8%). It turns green on exposure to the air, as do its solutions in all solvents. With acetone and alkali an indigotin derivative is obtained. The p-*nitrophenylhydrazone* consists of bright yellow, stout needles, m. p. 268—270°.

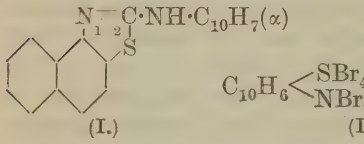
The author is indebted to the Research Fund Committee of the Chemical Society which has defrayed some of the expenses of this investigation.

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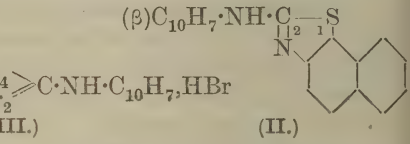
CCCXII.—*Aminobenzthiazoles. Part II. Naphthylaminonaphthathiazole Derivatives.*

By Robert Fergus Hunter.

The curious observations on the conversion of symmetrical diarylthiocarbamides into arylaminobenzthiazole bromides recorded in Part I (this vol., p. 2023) made it of interest to extend the investigation to the halogen derivatives of the naphthalene homologues of 1-anilinobenzthiazole (I and II), and the bromination of the *s*-dinaphthylthiocarbamides in chloroform was therefore studied.



(I.) (III.)



(II.)

Under conditions analogous to those employed in the previous cases (*loc. cit.*), *s*-di-α-naphthylthiocarbamide readily passed into the *tetrabromo*-addition compound of 2-α-naphthylamino-β-naphthathiazole (I), a substance having properties analogous to those of the tetrabromides described in Part I. On exposure to air it rapidly lost bromine, yielding a yellowish-orange *tribromide*; this, however, was not so stable as the tribromides of the benzenoid series, since it gradually lost bromine on exposure to the atmosphere. On treatment with sulphurous acid, the tetrabromide was rapidly reduced, the added bromine being eliminated as hydrogen bromide, and the free *base* (I) formed. The tetrabromide was converted by boiling hydroxylic solvents and alkalis into a *dibromo*-substitution derivative of the usual type (*loc. cit.*). The tetrabromide differs from those of the benzenoid series in that it is capable of uniting with hydrogen bromide and more bromine, yielding a *heptabromide*, which no doubt has the constitution (III), analogous to that of the *m*-toluthiazole heptabromide (*loc. cit.*).

On one occasion, when bromine was added to a warm suspension of di-α-naphthylthiocarbamide in chloroform, a bright red, unstable tribromo-addition compound was isolated, which was probably the hydrobromide of a dibromo-addition compound.

Since the bromination of *s*-di-α-naphthylthiocarbamide yielded as many as three bromo-addition compounds and was complicated by the tendency of the nascent thiazole to add on hydrogen bromide as well as bromine, the bromination of the naphthathiazole base itself was examined; as might have been anticipated, in

presence of excess of halogen it yielded a well-defined *hexabromide* the most probable constitution of which is

$$C_{10}H_6<\begin{matrix}SBr_4\\NBr_2\end{matrix}>C\cdot NHC_{10}H_7.$$

This compound has the usual properties of losing bromine on exposure to air, being reduced by sulphurous acid, and passing into the substitution product in presence of hydroxylic solvents and alkalis.

On bromination under similar conditions to those used in the case of the α-compound, *s*-di-β-naphthylthiocarbamide readily yielded a dark purplish-red *hexabromide* of (II), which doubtless is similar to the α-hexabromide in constitution. The β-hexabromide was isolated in two forms having identical chemical properties but different melting points. It differs from the higher bromo-addition compounds of the arylaminobenzthiazole series in being remarkably stable to air, in this respect resembling dehydrothio-toluidine dibromide (this vol., p. 1318); unlike this, however, it is decomposed by dilute alkalis and hydroxylic solvents. On treatment with sulphurous acid, the six bromine atoms are eliminated in the usual way with the liberation of (II). The direct elimination of bromine by treatment with hydroxylic solvents and alkalis had previously been observed in the case of 1 : 1-bisbenzthiazole tetrabromide (this vol., p. 1319), but this is a highly unstable substance which completely loses the whole of its added bromine on exposure to the air for some hours.

A *tribromo*-addition compound of 2-β-naphthylamino-α-naphthathiazole was also isolated, which resembled the hexabromide in its remarkable stability to air; on treatment with hydroxylic solvents and alkalis, however, the added bromine was eliminated (initially) as sodium hypobromite, with liberation of the thiazole base (II). The tribromide was reduced in the usual way by sulphurous acid, being no doubt the hydrobromide of the dibromo-addition compound of the thiazole.

The bromination of 2-β-naphthylamino-α-naphthathiazole in chloroform yielded, as might have been anticipated, the hexabromo-addition compound.

The bromine addition compounds of β-naphthylamino-α-naphthathiazole therefore differ from those of α-naphthylamino-β-naphthathiazole and of the arylaminobenzthiazoles (1) in their stability in air, which is of the order of that of dehydrothiotoluidine dibromide, (2) in losing their added halogen as hypobromite, with regeneration of the α-thiazole base, on treatment with hydroxylic solvents and alkalis, and (3) in being incapable of conversion into a stable, yellowish-orange tribromide by atmospheric oxidation.

Experimental.

s-Di-α-naphthylthiocarbamide was prepared from α-naphthylamine by the usual method (Hofmann, *Annalen*, 1846, **57**, 256). The crude product, after treatment with dilute acid, water, etc., was digested with boiling acetic acid and with boiling alcohol; the microcrystalline powder thus obtained had m. p. 196°; a further quantity slowly separated in prisms from the acetic acid filtrate.

2-α-*Naphthylamino*-β-*naphthathiazole Tetrabromide.* — Di-α-naphthylthiocarbamide (2 g.) was suspended in 20 c.c. of chloroform, and 2 c.c. of bromine were slowly added with continuous shaking; heat and hydrogen bromide were evolved towards the end of the bromination. The solution was refluxed for 2 minutes on a steam-bath and cooled in a freezing mixture; the *tetrabromide* then separated in minute, brilliant vermilion crystals, which were dried in a vacuum over potassium hydroxide. The tetrabromide lightened in colour at 190°, became yellow at 200°, and colourless at 260° (Found: Br, 50·2. $C_{21}H_{14}N_2Br_4S$ requires Br, 49·6%).

On exposure to air the tetrabromide lost bromine, yielding a yellowish-orange, crystalline mass of the *tribromide*, which after boiling with chloroform and drying in a vacuum was obtained in small, yellow prisms; these became pale at 200° and colourless at 280° [Found: Br, 42·6. $(C_{21}H_{14}N_2Br_3S)_2$ requires Br, 42·4%]. On treatment with sulphurous acid, the tribromide yielded the thiazole base in the usual way.

2-α-*Naphthylamino*-β-*naphthathiazole Heptabromide.*—By using 1 g. of *s*-di-α-naphthylthiocarbamide, 6 c.c. of chloroform, and 1 c.c. of bromine diluted with a little chloroform, and proceeding as in the previous bromination, bright red granules of a *heptabromide* (III) were obtained which lost bromine and became yellow at 160° (Found: Br, 62·6. $C_{21}H_{15}N_2Br_7S$ requires Br, 62·9%). This displayed the usual behaviour of the bromo-addition compounds on exposure to air, on treatment with sulphurous acid and on boiling with alcohol and subsequent treatment with sodium hydroxide.

Dibromo-2-α-*naphthylamino*-β-*naphthathiazole.* — Either of the above bromides (1 g.) was digested with 20 c.c. of boiling alcohol for a short time, the crystalline hydrobromide so obtained was treated with warm 2*N*-sodium hydroxide for a few minutes, the product washed, dried, and crystallised from benzene–ethyl acetate (1 : 1); from this the *dibromo*-substitution product separated in small prisms which sintered at 180°, became yellow at 240°, and melted at 270—272° (Found: Br, 35·9. $C_{21}H_{12}N_2Br_2S$ requires Br, 35·6%).

Red Tribromide of 2-α-*Naphthylamino*-β-*naphthathiazole*.—A suspension of 1 g. of the dinaphthylthiocarbamide in 6 c.c. of warm chloroform was treated with 1 c.c. of bromine diluted with a little chloroform; the yellow, crystalline precipitate that formed at the half stage turned red when the addition of the bromine was completed. The mixture was boiled for a minute, cooled, and the vermilion, microcrystalline precipitate dried in a vacuum over potassium hydroxide. The *tribromide* became orange at 180°, yellow at 190°, pale ochre-yellow at 215°, and showed signs of softening at 260°, but was still unmelted above 280° (Found: Br, 41·8. $C_{21}H_{14}N_2Br_2S,HBr$ requires Br, 42·4%). This tribromide lost bromine on exposure to air and was reduced by sulphurous acid in the usual way.

2-α-*Naphthylamino*-β-*naphthathiazole*.—Any one of the bromo-addition products obtained from the dinaphthylthiocarbamide by bromination in chloroform was suspended in sulphurous acid, and sulphur dioxide passed through the mixture until all solid matter was colourless. The reduction product was collected, digested with 2*N*-sodium hydroxide on a steam-bath for a few minutes, and the product washed, dried, and crystallised from ethyl acetate–toluene (1 : 1). The *naphthathiazole*, which separated in hard prisms, m. p. 217°, was recrystallised from benzene–ethyl acetate and obtained in colourless prisms, m. p. 221° (Found: S, 9·6. $C_{21}H_{14}N_2S$ requires S, 9·8%).

Bromination. From a solution of the naphthathiazole (0·3 g.) and bromine (0·5 c.c.) in chloroform, bright red prisms of the *hexabromide* separated slowly; they were dried in the usual way (Found: Br, 60·3. $C_{21}H_{14}N_2Br_6S$ requires Br, 59·6%). The hexabromide showed colour change without melting at 238° and behaved as usual on exposure to air and on treatment with sulphurous acid and with alcohol and sodium hydroxide.

s-Di-β-naphthylthiocarbamide was prepared from β-naphthylamine in the usual way. In the first experiments the thiocarbamide was recrystallised from glacial acetic acid, from which it separated in small prisms, m. p. 194°; in later experiments the product was treated as in the previous case and obtained as a micro-crystalline, white powder, m. p. 198°.

2-β-*Naphthylamino*-α-*naphthathiazole Hexabromide*.—(A) *s*-Di-β-naphthylthiocarbamide (m. p. 194°) (1 g.) containing a trace of acetic acid was suspended in 6 c.c. of chloroform and treated with 1 c.c. of bromine diluted with a small quantity of the same solvent as in the previous cases; the clear dark brown solution obtained became hot and evolved hydrogen bromide. The solution was refluxed for 2 minutes and cooled in a freezing mixture; the *hexa-*

bromide which then separated in fine, dark red crystals was dried in a vacuum over potassium hydroxide. It became light yellow at 190°, soft at 210°, and decomposed without melting at 216° (Found : Br, 60·3. $C_{21}H_{14}N_2Br_6S$ requires Br, 59·6%).

(B) The above bromination was repeated and the solution shaken to induce sudden crystallisation. The product consisted of small, purplish-red plates, which were dried in a vacuum as before. This hexabromide showed lightening in colour at 140°, further colour change at 194°, and melted to a clear red liquid at 196° (Found : Br, 59·8%).

Both forms of the hexabromide were reduced by sulphurous acid in the usual way, and exhibited the remarkable stability in air already referred to.

2-β-*Naphthylamino*-α-*naphthathiazole*.—The hexabromide was suspended in sulphurous acid and treated with a current of sulphur dioxide as in the previous case. The product was warmed with 2*N*-sodium hydroxide, washed, dried, and crystallised from toluene–ethyl acetate (1 : 1), from which it separated in large, silky plates, m. p. 221°. After recrystallisation from ethyl acetate–benzene, it was obtained in plates, m. p. 223° (Found : S, 8·9. $C_{21}H_{14}N_2S$ requires S, 9·8%).

Red Tribromide of 2-β-*Naphthylamino*-α-*naphthathiazole*.—One g. of *s*-di-β-naphthylthiocarbamide (microcrystalline powder, m. p. 198°) was suspended in 6 c.c. of chloroform and brominated in the usual way. The solution deposited the *tribromide* as a vermilion, microcrystalline powder which, after drying in a vacuum over potassium hydroxide, showed a colour change at about 170° and melted at 245° (Found : Br, 42·8. $C_{21}H_{14}N_2Br_2S,HBr$ requires Br, 42·4%).

Bromination of 2-β-*Naphthylamino*-α-*naphthathiazole*. — The naphthathiazole (0·5 g.) was treated with excess of bromine (1 c.c.) as in the previous case : on scratching, the hexabromide separated in small, dark purple-red prisms, m. p. 198°, after drying (Found : Br, 60·2. Calc., Br, 59·6%).

In conclusion, the author desires to express his gratitude to Prof. J. F. Thorpe, F.R.S., for the kind interest he has taken in the progress of these experiments.

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LONDON, S.W. 7. [*Received, June 3rd*, 1925.]

CCCXIII.—*An Investigation of the Action of Halogens on 2 : 4-Dimethylbenzoyl Chloride.*

By William Henry Perkin, jun., and John Frederic Smerdon Stone.

In a communication published a short time since (J., 1922, **121**, 2203), Davies and Perkin showed that ω-derivatives of the toluic acids such as

$$C_6H_4<\begin{matrix}CH_2X\\CO_2H\end{matrix} \qquad C_6H_4<\begin{matrix}CHX_2\\CO_2H\end{matrix} \qquad C_6H_4<\begin{matrix}CX_3\\CO_2H\end{matrix}$$

may be conveniently prepared from the corresponding toluoyl chlorides, $CH_3{\cdot}C_6H_4{\cdot}COCl$, or bromides by treatment with chlorine or bromine at temperatures varying from 160—220°, according to the degree of substitution desired, and subsequent decomposition of the substituted acid chlorides or bromides by formic acid, methyl alcohol, amines, etc. This simple process has made it possible to prepare conveniently many mono- and di-substitution derivatives of benzoic acid, such, for example, as the aldehydo-acids $CHO{\cdot}C_6H_4{\cdot}CO_2H$, which had previously been difficult of access.

In developing this process, it became interesting to determine the course substitution would take in the case of the dimethylbenzoic acids, $(CH_3)_2C_6H_3{\cdot}CO_2H$, that is to say, to find out whether substitution would occur in both methyl groups or be confined to one, and whether it would be possible, by the selection of suitable conditions of temperature, exposure to light, etc., to prevent simultaneous substitution in the ring. In order to examine this problem, we selected in the first instance 2 : 4-dimethylbenzoic acid (*m*-xylene-*o*-carboxylic acid) for investigation, and, as no method was available for the preparation of the large quantities of this acid required for this research, we have worked out the conditions most favourable for its formation. As the result of a large number of comparative experiments, we find that this acid may be obtained from *m*-xylene in a yield of 65% of that theoretically possible under the following conditions. *m*-Xylene is first converted, by acetyl chloride in the presence of anhydrous ferric chloride (compare Meissel, *Ber.*, 1899, **32**, 2420), into 2 : 4-dimethylacetophenone, $C_6H_3Me_2{\cdot}CO{\cdot}CH_3$, which, when treated with the calculated quantity of carefully prepared sodium hypobromite, is smoothly converted into practically pure 2 : 4-dimethylbenzoic acid. If, however, the hypobromite is present in excess or contains bromate, the acid is contaminated with a bromo-acid, m. p. 180°, which is evidently the 6-bromo-2 : 4-dimethylbenzoic acid,

m. p. 183—184°, obtained by Noyes (*Amer. Chem. J.*, 1898, 20, 802) by the oxidation of 6-bromo-2 : 4-dimethylacetophenone.

The method used for the direct substitution in the ω-positions in 2 : 4-dimethylbenzoic acid is essentially that worked out by Davies and Perkin (*loc. cit.*) in the case of the toluic acids. The acid is first converted into the acid chloride, $C_6H_3Me_2\cdot COCl$, by the action of thionyl chloride, and this is then treated with chlorine or bromine at temperatures varying from 160—220° according to the degree of substitution desired. The formation of the lower halogen substitution products takes place readily in bright sunlight but, if several atoms of chlorine or bromine are to be introduced, the use of a quartz mercury lamp is essential. In some cases, the bromo-derivatives were more readily prepared and separated than the corresponding chloro-derivatives.

Thus, for example, while we were unsuccessful in separating the ω-chloro- and ωω-dichloro-dimethylbenzoyl chlorides by fractional distillation, we found that the corresponding dibromo-derivatives, owing to greater difference in boiling point, could be comparatively easily separated. Careful treatment of the substituted acid chlorides with formic acid, alcohols or amines readily leads to the corresponding acids, esters, or amides. In this way we have prepared a large number of ω-halogen derivatives of 2 : 4-dimethylbenzoic acid, and the hydrolysis of these has yielded an interesting series of substances in which the methyl groups have been successively oxidised with production of alcohols, aldehydes, and acids.

I. *The ω-Bromo-2 : 4-dimethylbenzoic Acids.*

When 2 : 4-dimethylbenzoyl chloride is brominated at 160° with the aid of a mercury lamp, the bromo-acid bromide, distilling at 169—171°/15 mm., consists mainly of *2-bromomethyl-4-methylbenzoyl bromide*, $CH_3\cdot C_6H_3(CH_2Br)\cdot COBr$, but the fraction 160—180°/15 mm. contains this substance and *4-bromomethyl-2-methylbenzoyl bromide*, $CH_2Br\cdot C_6H_3(CH_3)\cdot COBr$, in the proportion of about 85 to 15%.*

On decomposing with formic acid, this mixture yields *2-bromomethyl-4-methylbenzoic acid*, m. p. 143—145°, the constitution of which is demonstrated by the fact that it yields *4-methyl-1 : 2-phthalide*, m. p. 118°, $CH_3\cdot C_6H_3<\begin{matrix}CH_2\\CO\end{matrix}>O$, at the melting point.

* In order to economise space, the formulæ in this communication are not written out hexagonally but the methyl-carbon atom to the left in the formula $CH_3\cdot C_6H_3(CH_3)\cdot CO_2H$ is numbered 4, whereas that to the right is numbered 2.

When an acid chloride is treated with bromine, it is converted into the acid bromide as pointed out by Davies and Perkin (*loc. cit.*, p. 2203).

The crystalline methyl ester (m. p. 62—63°) obtained directly by decomposing the mixed acid bromides with methyl alcohol is *methyl 2-bromomethyl-4-methylbenzoate*, because it decomposes on boiling into methyl bromide and 4-methyl-1 : 2-phthalide. This phthalide, on hydrolysis with alkali yields *2-hydroxymethyl-4-methylbenzoic acid*, which melts at 132—133° with regeneration of the phthalide.

The *methyl* ester of *4-bromomethyl-2-methylbenzoic acid* (m. p. 56°) is obtained by decomposing the mixed bromomethyl-methylbenzoyl bromides (see above) with methyl alcohol and boiling the mixed methyl esters, when methyl 2-bromomethyl-4-methylbenzoate passes completely into the phthalide whereas methyl 4-bromomethyl-2-methylbenzoate remains unchanged. On boiling with potassium hydroxide, the latter yields *4-hydroxymethyl-2-methylbenzoic acid*, $OH{\cdot}CH_2{\cdot}C_6H_3(CH_3){\cdot}CO_2H$, m. p. 142°, which does not lose water at its melting point. During this hydrolysis, a dibasic acid, $C_{18}H_{18}O_5$, m. p. 222°, is also obtained in small quantity and this is evidently *4 : 4′-dicarboxy-3 : 3′-dimethyldibenzyl ether*, $CO_2H{\cdot}(CH_3)C_6H_3{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}C_6H_3(CH_3){\cdot}CO_2H$, produced by the elimination of water from two molecules of the 4-hydroxymethyl acid. A somewhat similar observation was made by Günther (*Ber.*, 1890, **23**, 1061), who found that, when *p*-cyanobenzyl chloride, $CN{\cdot}C_6H_4{\cdot}CH_2Cl$, is hydrolysed with alkali, it yields 4 : 4′-dicarboxydibenzyl ether, $CO_2H{\cdot}C_6H_4{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2H$.

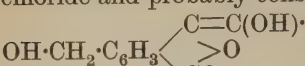
II. 2 : 4-*Di(bromomethyl)benzoic Acid*, $CH_2Br{\cdot}C_6H_3(CH_2Br){\cdot}CO_2H$.

The substitution of two atoms of bromine for hydrogen in 2 : 4-dimethylbenzoic acid leads mainly (compare p. 2286) to the formation of the *sym*-ω-dibromo-acid. The acid bromide of this acid, b. p. 223—228°/15 mm., is obtained when 2 : 4-dimethylbenzoyl chloride is heated with the calculated amount of bromine at a temperature rising from 150—190°, with the aid of the mercury lamp. On treatment with formic acid, this yields *2 : 4-di(bromomethyl)benzoic acid*, m. p. 158°, the methyl ester of which, on distillation, loses methyl bromide with the formation of *4-bromomethyl-1 : 2-phthalide*, $CH_2Br{\cdot}C_6H_3{<}\begin{matrix}CH_2\\CO\end{matrix}{>}O$, m. p. 159°, and this, on boiling with chalk and water, passes into *4-hydroxymethyl-1 : 2-phthalide*,

$$OH{\cdot}CH_2{\cdot}C_6H_3{<}\begin{matrix}CH_2\\CO\end{matrix}{>}O,$$

m. p. 125°. This substance is readily hydrolysed by warm sodium hydroxide to *2 : 4-di(hydroxymethyl)benzoic acid*, m. p. 146°. 4-Hydroxymethyl-1 : 2-phthalide condenses readily with oxalic ester in the presence of potassium ethoxide, yielding *4-hydroxymethyl-*

1 : 2-*phthalide-oxalic ester*, which gives a violet coloration with ferric chloride and probably consists essentially of the enolic modification,



In order to determine whether both bromine atoms in 2 : 4-di-(bromomethyl)benzoic acid are replaceable by cyanogen groups, the acid was digested with excess of potassium cyanide, but examination of the product showed that only the 4-ω-bromo-atom had been replaced by cyanogen, the product being 4-*cyanomethyl*-1 : 2-*phthalide*, m. p. 124°, $CN\cdot CH_2\cdot C_6H_3<\begin{matrix}CH_2\\CO\end{matrix}>O$. This on shaking with hydrogen peroxide and sodium hydroxide yields the *amide*, from which 1 : 2-*phthalide*-4-*acetic acid*, m. p. 162°,

$$CO_2H\cdot CH_2\cdot C_6H_3<\begin{matrix}CH_2\\CO\end{matrix}>O,$$

is obtained by the action of sodium nitrite.

III. *The Chlorination of* 2 : 4-*Dimethylbenzoyl Chloride.*

The attempt to prepare in a pure condition higher brominated derivatives of 2 : 4-dimethylbenzoic acid than those described in the last Section failed, mainly for the reason that the higher brominated acid bromides suffered vigorous decomposition when the attempt was made to distil them even under low pressures. Attention was therefore directed to the corresponding chloro-derivatives and we have fortunately been able to isolate these even up to the stage of the hexachloro-acid chloride, $CCl_3\cdot C_6H_3(CCl_3)\cdot COCl$. This has enabled us to study the whole series of these interesting substances and to investigate thoroughly their decomposition products and especially the products of their hydrolysis.

When 2 : 4-dimethylbenzoyl chloride is treated with the calculated amount of chlorine for the introduction of three atoms at a temperature rising from 180—210° and in ultra-violet light, and the product distilled, a fraction is obtained, b. p. 184—186°/16 mm., the chlorine content of which corresponds with that of the expected ω-trichloro-2 : 4-dimethylbenzoyl chloride. The first suspicion that this fraction is in reality an almost constant-boiling mixture of the di- and tetra-chlorinated dimethylbenzoyl chlorides, $CH_2Cl\cdot C_6H_3(CH_2Cl)\cdot COCl$ and

$$CHCl_2\cdot C_6H_3(CHCl_2)\cdot COCl,$$

containing only small quantities of the trichlorinated derivative, arose on attempting to prepare the substituted chlorophthalides by boiling the corresponding methyl esters. When the methyl esters, prepared in the usual manner from the acid chloride

fraction and methyl alcohol, are distilled, the crystals which separate from the distillate consist of 4-*chloromethyl*-1 : 2-*phthalide*, $CH_2Cl\cdot C_6H_3<\begin{matrix}CH_2\\CO\end{matrix}>O$, m. p. 144°, derived from the methyl ester, $CH_2Cl\cdot C_6H_3(CH_2Cl)\cdot CO_2Me$, and corresponding with the 4-bromomethyl-1 : 2-phthalide described on p. 2277, the yield being about 30%. On the other hand, when the chloride fraction, b. p. 184—186°/16 mm., was digested with chalk and water, it gave a large yield of 2 : 4-dialdehydobenzoic acid, $CHO\cdot C_6H_3(CHO)\cdot CO_2H$, an interesting substance which had not previously been obtained and the properties of which are described on p. 2290. The formation of this dialdehydo-acid is clear evidence that the acid chloride must have contained considerable quantities of 2 : 4-di(dichloromethyl)benzoyl chloride, $CHCl_2\cdot C_6H_3(CHCl_2)\cdot COCl$. That the acid chloride fraction also contains 4-dichloromethyl-2-chloromethylbenzoyl chloride, $CHCl_2\cdot C_6H_3(CH_2Cl)\cdot COCl$, was demonstrated in the following manner. The product of the action of chalk and water on this chloride fraction contains, besides 2 : 4-dialdehydobenzoic acid, a small quantity of a substance, $C_9H_6O_3$, melting at 159—160°, which, on investigation, proved to be 4-*aldehydo*-1 : 2-*phthalide*, $CHO\cdot C_6H_3<\begin{matrix}CH_2\\CO\end{matrix}>O$, and this must have been derived from the trichloro-acid chloride just mentioned. On the other hand, there is no evidence of the existence of the isomeric trichloro-acid chloride, $CH_2Cl\cdot C_6H_3(CHCl_2)\cdot COCl$, in the above chloride fraction, because careful examination of the products of hydrolysis with chalk and water failed to reveal the presence of any substance derived from this chloride.

4-Aldehydo-1 : 2-phthalide combines readily with phenylhydrazine, yielding the yellow *hydrazone*, $PhN_2H{:}CH\cdot C_6H_3<\begin{matrix}CH_2\\CO\end{matrix}>O$, but its most interesting property is the fact that, when heated on the steam-bath even with 2*N*-sodium hydroxide, it undergoes the Cannizzaro reaction and yields a mixture of 2 : 4-di(hydroxymethyl)benzoic acid, $OH\cdot CH_2\cdot C_6H_3(CH_2\cdot OH)\cdot CO_2H$ (m. p. 146°; compare p. 2290), and 2-*hydroxymethylterephthalic acid*,

$$CO_2H\cdot C_6H_3(CH_2\cdot OH)\cdot CO_2H.$$

On heating in the steam-oven, the latter acid is converted into 4-*carboxy*-1 : 2-*phthalide*, $CO_2H\cdot C_6H_3<\begin{matrix}CH_2\\CO\end{matrix}>O$, m. p. 280°, a substance which is readily reconverted into 2-hydroxymethylterephthalic acid on hydrolysis.

IV. 2 : 4-*Di*(*dichloromethyl*)*benzoic Acid.*

When 2 : 4-dimethylbenzoyl chloride is chlorinated at 160—220° in ultra-violet light, until the increase of weight corresponds with the introduction of 4 atoms of chlorine, and the product fractionated, 2 : 4-*di*(*dichloromethyl*)*benzoyl chloride*,

$$CHCl_2 \cdot C_6H_3(CHCl_2) \cdot COCl,$$

b. p. 192—193°/10 mm., is obtained in good yield. Unlike the lower chlorinated dimethylbenzoyl chlorides, this substance is remarkably resistant to moisture and may be left exposed to air for some days without appreciable decomposition but it is decomposed by anhydrous formic acid under carefully regulated conditions to yield 2 : 4-*di*(*dichloromethyl*)*benzoic acid*, m. p. 160°. The *methyl* ester of this acid, $CHCl_2 \cdot C_6H_3(CHCl_2) \cdot CO_2Me$, distils at 186—188°/12 mm. without decomposition, but, at higher temperatures, it loses methyl chloride with the formation of 4-*dichloromethyl*-1 : 2-*chlorophthalide*, $CHCl_2 \cdot C_6H_3 < \begin{matrix} CHCl \\ CO \end{matrix} > O$, an oil distilling at 297°/763 mm. When 2 : 4-di(dichloromethyl)benzoyl chloride is boiled with chalk and water, it is converted into 2 : 4-*dialdehydobenzoic acid*, $CHO \cdot C_6H_3(CHO) \cdot CO_2H$, m. p. 141° (compare p. 2292). The yield of this important new acid, which appears to be the first of the dialdehydobenzoic acids to be prepared, calculated on the weight of the chloride employed in its preparation, is at least 70% of the theoretical. On treatment with aniline, it yields a *dianilino*-derivative which, since it is insoluble in sodium carbonate, probably has the constitution $NPh{:}CH \cdot C_6H_3 < \begin{matrix} CH \cdot NHPh \\ CO \end{matrix} > O$, the acid having acted in its hydroxy-phthalide modification much in the same way as *m*-opianic acid does in the same circumstances (Fargher and Perkin, J., 1921, 119, 1729). The *disemicarbazone* is colloidal and could not be crystallised. It decomposes at 335° and is soluble in sodium carbonate, consequently it appears to be directly derived from the dialdehydo-acid and to have the normal constitution.

2 : 4-Dialdehydobenzoic acid reacts readily with phenylhydrazine to yield a yellow, crystalline derivative, m. p. 266°, insoluble in sodium carbonate, which is evidently *anhydro*-2 : 4-*dialdehydobenzoic acid diphenylhydrazone*, $PhN_2H{:}CH \cdot C_6H_3 < \begin{matrix} CH{:}N \\ CO \cdot NPh \end{matrix}$. It is proposed to investigate carefully the action of alkalis on 2 : 4-dialdehydobenzoic acid, in order to determine whether one or both of the aldehydo-groups are susceptible to the Cannizzaro reaction.

V. *The Pentachloro-2 : 4-dimethylbenzoyl Chlorides.*

An acid chloride fraction, b. p. 188—192°/14 mm., is obtained when chlorine is passed into 2 : 4-dimethylbenzoyl chloride, in the presence of ultra-violet light, at 220° until the increase in weight corresponds with the absorption of five atoms of chlorine. Investigation of this product has proved that it contains about equal quantities of the isomeric chlorides, $CCl_3 \cdot C_6H_3(CHCl_2) \cdot COCl$ and $CHCl_2 \cdot C_6H_3(CCl_3) \cdot COCl$. On hydrolysis with chalk and water, this mixture yields a sparingly soluble, crystalline acid, m. p. 242°, which examination has proved to be *2-aldehydoterephthalic acid*, $CO_2H \cdot C_6H_3(CHO) \cdot CO_2H$. This new acid reacts readily with phenylhydrazine with the formation of a colourless substance, $C_{15}H_{10}O_3N_2$, m. p. 327°, which is evidently *anhydro-2-aldehydoterephthalic acid phenylhydrazone*, $CO_2H \cdot C_6H_3 < \begin{matrix} CH{:}N \\ CO \cdot NPh \end{matrix}$. On treatment with hydroxylamine, 2-aldehydoterephthalic acid yields the normal *oxime*, $CO_2H \cdot C_6H_3(CH{:}N \cdot OH) \cdot CO_2H$, and, on heating, this melts and decomposes at about 136° with evolution of heat, solidifies again, and then melts at about 242°, isomeric change into the *imide* of *trimellitic acid*, a substance which does not appear to have been described, taking place. This characteristic change is analogous to the conversion by heat of the oximes of opianic acid and *ψ*-opianic acid into hemipinimide (Liebermann, *Ber.*, 1886, **19**, 2926; Perkin, J., 1890, **57**, 1071) and of the oxime of *m*-opianic acid into *m*-hemipinimide (Perkin, J., 1916, **109**, 930). 2-Aldehydoterephthalic acid does not undergo the Cannizzaro reaction so readily as 4-aldehydo-1 : 2-phthalide (p. 2279), but when boiled with sodium hydroxide (25%) it is converted into a mixture of *2-hydroxymethylterephthalic acid*, $CO_2H \cdot C_6H_3(CH_2 \cdot OH) \cdot CO_2H$, and trimellitic acid, $CO_2H \cdot C_6H_3(CO_2H) \cdot CO_2H$.

The mother-liquors from which the 2-aldehydoterephthalic acid had separated contain, besides this acid, varying quantities of trimellitic acid produced evidently by the air oxidation of the aldehydo-acid and probably also of the isomeric *4-aldehydophthalic acid*, $CHO \cdot C_6H_3(CO_2H) \cdot CO_2H$. This latter acid is contained in these mother-liquors in considerable quantity, although, owing to its ready solubility and small facility for crystallising, it has not yet been found possible to isolate it in a pure condition.

The presence of this interesting isomeride of 2-aldehydoterephthalic acid was demonstrated in the first place by treating the impure acid with phenylhydrazine, when a substance crystallising in yellow needles, m. p. 118°, was isolated in quantity; this is readily soluble in sodium carbonate and consists of the *hydrate* of the

phenylhydrazone of 4-*aldehydophthalic acid*, $C_{15}H_{12}O_4N_2,H_2O$. This characteristic substance becomes anhydrous in a vacuum desiccator over sulphuric acid, melts at 174° with elimination of water and formation of the *anhydride*, $PhN_2H{:}CH{\cdot}C_6H_3(CO)_2O$, m. p. 217°, and this anhydride formation takes place quantitatively on heating in the air-oven at 115°.

VI. 2 : 4-*Di*(*trichloromethyl*)*benzoic Acid*.

The chloride of this acid, $CCl_3{\cdot}C_6H_3(CCl_3){\cdot}COCl$, b. p. 192—196°/15 mm., is obtained as a colourless oil which does not fume in moist air and in a yield of 70—80% when 2 : 4-dimethylbenzoyl chloride is chlorinated in ultra-violet light at 220° until six chlorine atoms have been absorbed. The stability of this chloride is also demonstrated by its behaviour with alkalis, since it may be boiled for a short time with dilute sodium carbonate without dissolving, although some chlorine is eliminated from the side chain during the process.

However, on leaving with anhydrous formic acid for about 2 weeks at the ordinary temperature, hydrolysis gradually takes place and 2 : 4-*di*(*trichloromethyl*)*benzoic acid* is obtained in colourless needles, m. p. 171°. The *methyl* ester, $CCl_3{\cdot}C_6H_3(CCl_3){\cdot}CO_2Me$, obtained by mixing the hexachloro-acid chloride with methyl alcohol, does not crystallise and decomposes, on heating, with elimination of methyl chloride and formation of 4-*trichloromethylphthalyl chloride* of the probable formula $CCl_3{\cdot}C_6H_3{<}\begin{matrix}CCl_2\\CO\end{matrix}{>}O$. This interesting substance, b. p. 186—187°/12 mm., does not appear to be hydrolysed by anhydrous formic acid, but it reacts readily with aniline to yield a *dianilide* which crystallises in colourless needles, m. p. 220°, and appears to be 4-*trichloromethylphthaldianilide* and to have the constitution $CCl_3{\cdot}C_6H_3(CO{\cdot}NHPh)_2$. Although the hexachloride (see above) is so resistant to hydrolysis, it reacts readily with ammonia or with aniline and is gradually hydrolysed by chalk and water. Thus the *amide*, $CCl_3{\cdot}C_6H_3(CCl_3){\cdot}CO{\cdot}NH_2$, is obtained in colourless needles when dry ammonia is passed into the solution of the acid chloride in benzene. This amide melts at 176° with elimination of hydrogen chloride, due probably to the formation of the substance $CCl_3{\cdot}C_6H_3{<}\begin{matrix}CCl_2\\C{:}NH\end{matrix}{>}O,HCl$ (compare Gabriel and Landsberger, *Ber.*, 1898, **31**, 2732). The addition of aniline to the solution of the hexachloro-acid chloride in benzene yields the *anilide* of 2 : 4-*di*(*trichloromethyl*)*benzoic acid*,

$$CCl_3{\cdot}C_6H_3(CCl_3){\cdot}CO{\cdot}NHPh,$$

m. p. 203°. When the hexachloro-acid chloride is boiled with

chalk and water, gradual hydrolysis takes place, each $-CCl_3$ group becoming $-CO_2H$, and ultimately an almost quantitative yield of trimellitic acid, $CO_2H{\cdot}C_6H_3(CO_2H){\cdot}CO_2H$, is obtained.

Experimental.

2 : 4-*Dimethylacetophenone*, $CH_3{\cdot}C_6H_3(CH_3){\cdot}CO{\cdot}CH_3$.—Anhydrous ferric chloride (100 g.) is just covered with dry carbon disulphide in a 2-litre flask, fitted with a reflux condenser and dropping funnel, and a mixture of *m*-xylene (100 g.) and a slight excess of acetyl chloride (84 g.) is slowly run in with occasional vigorous shaking, the operation taking about ¾ hour. The whole is heated on the steam-bath until the evolution of hydrogen chloride ceases (approx. 2 hours), the thick dark liquid poured into water, and after addition of ether, the black ether layer is well washed with water and dilute sodium hydroxide, dried over calcium chloride, and the ether removed. Meissel (*Ber.*, 1899, **32**, 2420) recommends distilling the dark oil in steam, but this is unnecessary, since ordinary distillation suffices, the portion distilling at 220—230° being sufficiently pure for most purposes and on redistillation the pure ketone distils at 228°/760 mm. (Found : C, 81·0; H, 8·2. $C_{10}H_{12}O$ requires C, 81·0; H, 8·1%).

2 : 4-*Dimethylbenzoic Acid*, $CH_3{\cdot}C_6H_3(CH_3){\cdot}CO_2H$.—After several comparative experiments, the best oxidising agent for converting 2 : 4-dimethylacetophenone into this acid was found to be sodium hypobromite, but unless the temperature is kept as near 0° as possible both in the preparation of the hypobromite and in the subsequent oxidation, a brominated 2 : 4-dimethylbenzoic acid is also obtained which melts at 180° and is apparently identical with the 6-bromo-2 : 4-dimethylbenzoic acid, m. p. 183—184°, described by Noyes (*Amer. Chem. J.*, 1898, **20**, 802) (Found : C, 47·1; H, 4·1. $C_9H_9O_2Br$ requires C, 47·2; H, 3·9%). Sodium hydroxide (80 g.) is dissolved in water (1600 c.c.) cooled to 0°, and then bromine (160 g.) carefully run in in small quantities with vigorous shaking, 2 : 4-dimethylacetophenone (50 g.) is now added and the whole shaken continuously for 2 hours. The operation is seen to be at an end when the surface layer of the ketone gives place to a heavy layer of bromoform. After this has been run off, the aqueous solution is saturated with sulphur dioxide, when 2 : 4-dimethylbenzoic acid is precipitated as a voluminous, crystalline precipitate; after washing and drying, it is pure enough for most purposes. For the chlorination experiments it was, however, found better to recrystallise it from dilute alcohol, from which it separates in long needles, m. p. 126° (Found : C, 71·9; H, 6·8. $C_9H_{10}O_2$ requires C, 72·0; H, 6·7%).

The *methyl* ester, $CH_3 \cdot C_6H_3(CH_3) \cdot CO_2Me$, is readily prepared by adding the acid chloride (see below) to methyl alcohol and precipitating with water. The ether extract is well washed with water and sodium carbonate, dried over calcium chloride, the ether removed, and the oil distilled, when the methyl ester passes over at 232—233°/762 mm. and melts at — 2° to — 1° (Found: C, 73·0; H, 7·3. $C_{10}H_{12}O_2$ requires C, 73·2; H, 7·3%).

2-Bromomethyl-4-methylbenzoyl Bromide, $CH_3 \cdot C_6H_3(CH_2Br) \cdot COBr$. —The 2 : 4-dimethylbenzoyl chloride required in large quantities for this and the subsequent operations was obtained in a yield of 90% by boiling the acid with 10% excess of thionyl chloride. The dark oil remaining after distilling off the excess distilled at 234—236°/760 mm. or at 113—115°/15 mm. and melted at about 25·5° (compare Ador and Meier, *Ber.*, 1879, **18**, 1970). The bromination of this chloride is carried out in a flask fitted with a reflux condenser and dropping funnel the end of which is well below the surface of the chloride (33·7 g.). At 160°, bromine (32 g.) is slowly run in and, provided the operation is done in plenty of sunlight, substitution rarely takes more than an hour and the temperature need not be raised above 180°. In ultra-violet light double this quantity of the chloride can be brominated in an hour at a temperature not exceeding 160°. The separation and purification of this acid bromide is rendered tedious owing to the presence of small quantities of its isomeride, *4-bromomethyl-2-methylbenzoyl bromide*, $CH_2Br \cdot C_6H_3(CH_3) \cdot COBr$, which has not been obtained in a pure condition, although certain derivatives are described later in this paper. After three or four fractionations under reduced pressure, a yield of 50% of 2-bromomethyl-4-methylbenzoyl bromide, containing traces of the isomeride, is obtained as a slightly green oil distilling at 169—171°/15 mm. It is rapidly decomposed by moist air and should be used directly it has been prepared (Found: Br, 54·9. $C_9H_8OBr_2$ requires Br, 54·8%). In order to prove that this substance consisted entirely of bromo-acid bromide and did not contain any acid chloride, the silver halide (0·4386 g.) from the Carius determination was heated in a stream of chlorine at 200° for 2 hours, when 0·3496 AgCl resulted, whereas theory requires 0·3508. This fully confirms the observation of Davies and Perkin (*loc. cit.*) that acid chlorides are completely converted into acid bromides on treatment with bromine.

2-Bromomethyl-4-methylbenzoic Acid, $CH_3 \cdot C_6H_3(CH_2Br) \cdot CO_2H$.— This acid is readily obtained from the acid bromide by stirring with six times its weight of anhydrous formic acid, care being taken that the temperature does not rise above 15°, in order to avoid any hydrolysis of the side chain bromine atom. The operation

is complete in a few minutes and the precipitate of the acid is collected and crystallised from petroleum (b. p. 80—100°), from which it separates in small, colourless needles, m. p. 143—145° (decomp.) (Found : Br, 34·1. $C_9H_9O_2Br$ requires Br, 34·9%). The *methyl* ester, $CH_3{\cdot}C_6H_3(CH_2Br){\cdot}CO_2Me$, is obtained by adding the acid bromide to well-cooled methyl alcohol and, after standing over-night, the mixture is poured into water, ether added, and the ethereal extract well washed with water and dilute sodium carbonate, dried over anhydrous sodium sulphate, and evaporated. The syrup gradually crystallises in colourless needles which are drained and crystallised from petroleum, in which the substance is very soluble and from which it separates in rectangular prisms, m. p. 62—63° (Found : Br, 33·0. $C_{10}H_{11}O_2Br$ requires Br, 32·9%). The vapour of this methyl ester is very irritating and causes prolonged sneezing. When boiled in a test tube for a few minutes, it readily loses methyl bromide with formation of 4-*methyl*-1 : 2-*phthalide*, $CH_3{\cdot}C_6H_3{<}\overset{CH_2}{CO}{>}O$, in theoretical yield. The melt solidifies, on cooling, and the phthalide is best recrystallised from petroleum, from which it separates in long, colourless needles, m. p. 117—118° (Found : C, 72·9; H, 5·5. $C_9H_8O_2$ requires C, 72·9; H, 5·4%). This substance dissolves readily on boiling with dilute sodium hydroxide and, on the addition of hydrochloric acid to the cold solution, 2-*hydroxymethyl*-4-*methylbenzoic acid* separates in small needles (Found : C, 64·9; H, 5·9. $C_9H_{10}O_3$ requires C, 65·1; H, 6·0%). This acid melts at 132—133° with loss of water and regeneration of the phthalide.

Methyl 4-*Bromomethyl*-2-*methylbenzoate*, $CH_2Br{\cdot}C_6H_3(CH_3){\cdot}CO_2Me$. —Reference has already been made (p. 2276) to the presence in the acid bromide, prepared as explained above, of small quantities of 4-bromomethyl-2-methylbenzoyl bromide. Although it was found impossible to isolate this from the mixture, the methyl ester of the bromo-acid may be obtained pure in the following manner. The bromo-acid bromide fraction, b. p. 160—180°/15 mm., is converted into the mixture of methyl esters in the way just described, and the mixture boiled until all the methyl 2-bromomethyl-4-methylbenzoate has been converted, by loss of methyl bromide, into 4-methyl-1 : 2-phthalide. This separates almost completely on mixing with light petroleum, and the filtrate, on evaporation, deposits methyl 4-bromomethyl-2-methylbenzoate as a crystalline mass which crystallises from methyl alcohol in needles, m. p. 55—56°, and is readily distinguished from its isomeride in that, on boiling, it does not decompose with loss of methyl bromide (Found : Br, 31·2. $C_{10}H_{11}O_2Br$ requires Br, 32·9%).

4-*Hydroxymethyl*-2-*methylbenzoic Acid*, $OH{\cdot}CH_2{\cdot}C_6H_3(CH_3){\cdot}CO_2H$. —Complete hydrolysis of the above methyl ester (4·5 g.) is readily effected by boiling with potassium hydroxide (3 g. in 50 c.c. of water) for 2 hours. After filtering, the cold solution is acidified with concentrated hydrochloric acid, the voluminous crystalline precipitate collected and crystallised from boiling water, from which 4-*hydroxymethyl*-2-*methylbenzoic acid* separates in glistening, rectangular plates, m. p. 141—142° (Found: C, 65·3; H, 6·1. $C_9H_{10}O_3$ requires C, 65·1; H, 6·0%).

During the recrystallisation of this acid, a small quantity of a white substance remains undissolved and this separates from dilute alcohol as a microcrystalline powder, m. p. 221—222°. It is explained in the introduction (p. 2277) that this substance is 4 : 4′-*dicarboxy*-3 : 3′-*dimethyldibenzyl ether* (Found: C, 68·1; H, 5·7. $C_{18}H_{18}O_5$ requires C, 68·8; H, 5·7%). On titration, 0·0252 required 1·6 c.c. of N/10-NaOH for neutralisation, whereas this amount of a dibasic acid, $C_{18}H_{18}O_5$ should neutralise 1·6 c.c. The molecular weight, determined by the method of Rast (*Ber.*, 1922, **55**, 1051, 3727), when 0·0047, dissolved in 0·0859 of camphor, caused a depression in the m. p. of camphor of 6·9°, was found as 317, whereas $C_{18}H_{18}O_5$ requires M, 314.

2 : 4-*Di*(*bromomethyl*)*benzoyl Bromide*, $CH_2Br{\cdot}C_6H_3(CH_2Br){\cdot}COBr$. —The bromination of 2 : 4-dimethylbenzoyl bromide to this stage cannot be effected with good results in sunlight, but with the aid of a mercury lamp and careful regulation of the temperature a yield of 40—50% of the above bromide may be obtained. Starting with the temperature at 150°, bromine (106 g.) is slowly dropped into 2 : 4-dimethylbenzoyl chloride (56 g.), the operation being complete in 2 hours if the temperature at the end of the experiment is allowed to rise to 190°. Above this, considerable darkening of the liquid takes place and subsequent fractionation is rendered difficult owing to the formation of much tar. The dark green liquid is distilled in small quantities under reduced pressure as quickly as possible and the fraction 215—230°/15 mm. again distilled, when the fraction 223—228°/15 mm. consists of almost pure 2 : 4-di(bromomethyl)benzoyl bromide (Found: Br, 64·0. $C_9H_7OBr_3$ requires Br, 64·7%). This bromide is a viscid, green syrup which fumes in moist air and shows no signs of crystallising even on long standing.

2 : 4-*Di*(*bromomethyl*)*benzoic Acid*, $CH_2Br{\cdot}C_6H_3(CH_2Br){\cdot}CO_2H$.— This acid, prepared in the usual manner by stirring the acid bromide with anhydrous formic acid at as low a temperature as possible (p. 2284), crystallises from benzene in small, colourless prisms, m. p. 158° (Found: Br, 52·4. $C_9H_8O_2Br_2$ requires Br, 52·0%).

The *methyl* ester, obtained by adding the dibromo-acid bromide to well-cooled methyl alcohol, separates from the mixture and crystallises from methyl alcohol in long, colourless, feathery needles, m. p. 83—84° (Found : Br, 49·7. $C_{10}H_{10}O_2Br_2$ requires Br, 49·7%). The vapour of this methyl ester is very pungent and produces prolonged sneezing, and solutions cause burns when brought in contact with the skin. When this methyl ester is boiled in a test-tube for a few minutes, it loses methyl bromide, and the melt, on cooling, crystallises in fan-shaped masses of needles. This consists of nearly pure 4-*bromomethyl*-1 : 2-*phthalide*, $CH_2Br{\cdot}C_6H_3{<}\begin{matrix}CH_2\\CO\end{matrix}{>}O$, which separates from methyl alcohol in small, glistening plates, m. p. 159°, and is very pungent when warmed (Found : Br, 34·9. $C_9H_7O_2Br$ requires Br, 35·2%).

4-*Hydroxymethyl*-1 : 2-*phthalide*, $OH{\cdot}CH_2{\cdot}C_6H_3{<}\begin{matrix}CH_2\\CO\end{matrix}{>}O$. — This substance may be obtained by boiling 2 : 4-di(bromomethyl)benzoyl bromide with precipitated chalk and water, but the method is unsatisfactory owing to the difficulty in purifying the product. Subsequently it was found that a much better yield of pure substance can be obtained by boiling 4-bromomethyl-1 : 2-phthalide (5 g.) with chalk (2 g.) and water (50 c.c.). After cooling, the solution is acidified with hydrochloric acid and the whole quickly filtered, when the filtrate gradually deposits small, colourless prisms (2·5 g.). 4-*Hydroxymethyl*-1 : 2-*phthalide*, m. p. 124—125°, is readily soluble in hot water or toluene but sparingly so in cold water or ether (Found : C, 66·1; H, 4·9. $C_9H_8O_3$ requires C, 65·9; H, 4·9%).

2 : 4-*Di*(*hydroxymethyl*)*benzoic Acid*,

$$OH{\cdot}CH_2{\cdot}C_6H_3(CH_2{\cdot}OH){\cdot}CO_2H.$$

—This, the parent substance of the above hydroxymethylphthalide, is prepared by warming the latter with sodium hydroxide, cooling well, and acidifying with hydrochloric acid. After being quickly collected, washed with water, and left on porous porcelain exposed to air, the small, colourless, glistening plates melt at 145—146° (Found : C, 59·2; H, 5·6. $C_9H_{10}O_4$ requires C, 59·3; H, 5·5%).

Ethyl 4-*Hydroxymethyl*-1 : 2-*phthalideoxalate*,

$$OH{\cdot}CH_2{\cdot}C_6H_3{<}\begin{matrix}C{\cdot}C(OH){\cdot}CO_2Et\\{>}O\\CO\end{matrix}.$$

—In preparing this substance, absolute alcohol (0·4 c.c.) is carefully added to molecular potassium (0·4 g.) under dry ether (30 c.c.) and after the evolution of hydrogen has ceased and a slight excess of potassium is present, oxalic ester (1·5 g.) is added. Combination follows at once, the potassium ethoxide passes into solution and

the colour changes to yellow. Hydroxymethylphthalide (1·7 g.) suspended in dry ether is now added and the whole left over-night. The voluminous, yellow precipitate is collected, dissolved in a little water, and the orange solution of the potassium derivative acidified. The viscid oil which gradually crystallises separates from dilute alcohol in small, colourless prisms, m. p. 169—170° (Found: C, 59·3; H, 4·6. $C_{13}H_{12}O_6$ requires C, 59·1; H, 4·6%). The methyl-alcoholic solution gives, on the addition of ferric chloride, a deep violet coloration, and the substance is immediately soluble in sodium hydroxide to a yellow solution.

4-*Cyanomethyl*-1 : 2-*phthalide*, $CH_2(CN)\cdot C_6H_3<\begin{matrix}CH_2\\CO\end{matrix}>O$.—2 : 4-Di(bromomethyl)benzoic acid (25 g.) was gradually added to potassium cyanide (14 g.) dissolved in alcohol (50 c.c.) and water (100 c.c.) and, after the somewhat vigorous reaction had subsided, the whole was heated on the steam-bath for 10 minutes, cooled, and diluted with water (100 c.c.). The solution, acidified with hydrochloric acid, was extracted with ether, and the ethereal layer well washed with water and dried over calcium chloride, when a small quantity of a red gum separated. The ether was then removed from the filtered solution; the oil, which gradually solidified, separated from benzene in small plates, m. p. 123—124° (Found: C, 69·5; H, 4·1; N, 8·0. $C_{10}H_7O_2N$ requires C, 69·4; H, 4·0; N, 8·1%). 1 : 2-*Phthalide*-4-*acetamide* is readily prepared by shaking the cyano-derivative (3 g.) with hydrogen peroxide (30 c.c. of 6%) and sodium hydroxide (1 c.c. of 10%) at 40°. When all has dissolved and the evolution of oxygen has ceased, the solution is acidified with concentrated hydrochloric acid and the small, white plates are collected. This amide separates from alcohol in feathery needles, m. p. 218—219° (slight decomp.) (Found: C, 62·7; H, 4·8. $C_{10}H_9O_3N$ requires C, 62·8; H, 4·7%).

1 : 2-*Phthalide*-4-*acetic Acid*, $CO_2H\cdot CH_2\cdot C_6H_3<\begin{matrix}CH_2\\CO\end{matrix}>O$.—The hydrolysis of 4-cyanomethyl-1 : 2-phthalide by methyl-alcoholic potassium hydroxide yields a product which is difficult to purify, but the acid is readily obtained in a practically theoretical yield under the following conditions. The amide (0·24 g.) is dissolved in concentrated sulphuric acid and the whole heated on the steam-bath for a few minutes, cooled to 0°, and sodium nitrite (0·2 g.) dissolved in water (1 c.c.) added. After heating on the steam-bath for about 3 minutes, the product is poured into water (5 c.c.), when, on cooling, needles are deposited which are completely soluble in dilute sodium carbonate and, after recrystallisation from water, melt at 161—162° and consist of 1 : 2-phthalide-4-acetic

acid (Found : C, 62·3; H, 4·3. $C_{10}H_8O_4$ requires C, 62·5; H 4·2%).

The only indication that an unsymmetrical dibromo-derivative is formed during the bromination of 2 : 4-dimethylbenzoyl chloride was obtained when a large quantity of the dibrominated bromide (b. p. 215—230°/15 mm.) was hydrolysed with chalk and water (compare p. 2287).

On adding phenylhydrazine to the mother-liquor from which the 4-hydroxymethyl-1 : 2-phthalide had separated, a small quantity of a condensation product was obtained which crystallised from benzene–petroleum in small, yellow prisms, m. p. 179—180° (Found : C, 70·7; H, 5·4. $C_{15}H_{14}O_2N_2$ requires C, 70·8; H, 5·5%). This substance is evidently the phenylhydrazone either of $CHO{\cdot}C_6H_3(CH_3){\cdot}CO_2H$ or of $CH_3{\cdot}C_6H_3(CHO){\cdot}CO_2H$, probably the former, but the amount available was too small for further investigation.

Preparation of the Mixture of 2 : 4-*Di*(*chloromethyl*)- *and* 2 : 4-*Di*(*dichloromethyl*)*benzoyl Chlorides*, $CH_2Cl{\cdot}C_6H_3(CH_2Cl){\cdot}COCl$ and $CHCl_2{\cdot}C_6H_3(CHCl_2){\cdot}COCl$.—The apparatus employed in the preparation of all the chlorinated 2 : 4-dimethylbenzoyl chlorides described in this communication consisted of a quartz flask, of 300 c.c. capacity, having a wide neck about 12 inches long in which was fitted a cork bored with three holes for carrying a thermometer, an adapter for attaching to a reflux condenser, and a tube, for introducing the chlorine, reaching nearly to the bottom of the flask. The whole apparatus (without the condenser) with its contents could be weighed from time to time in order to determine the amount of chlorine absorbed, and chlorination was always carried out in close proximity to a powerful ultra-violet light mercury lamp.

When 2 : 4-dimethylbenzoyl chloride (p. 2284; 60 g.) was chlorinated under these conditions at a temperature starting at 180° and gradually rising to 210° until 3 atoms of chlorine had been absorbed, and the product fractionated, about 60% passed over at 184—186°/16 mm. as an almost colourless, fuming oil which gave analytical results corresponding with those required for a *trichloro-dimethylbenzoyl chloride* (Found : Cl, 51·7. $C_9H_6OCl_4$ requires Cl, 52·2%). As stated in the introduction (p. 2278), this oil is in reality a constant-boiling mixture consisting essentially of di- and tetra-chloro-acid chlorides and containing only a small quantity of the trichlorinated chloride. From this mixture the following derivatives were prepared.

4-*Chloromethyl*-1 : 2-*phthalide*, $CH_2Cl{\cdot}C_6H_3{<}^{CH_2}_{CO}{>}O$.—The mixed chlorides were converted into the mixed methyl esters by boiling with

methyl alcohol; these were isolated in the usual manner (p. 2285). When the resulting oil was heated to boiling in small quantities, the methyl ester, $CH_2Cl{\cdot}C_6H_3(CH_2Cl){\cdot}CO_2Me$, readily decomposed * with elimination of methyl chloride and formation of solid 4-chloromethyl-1 : 2-phthalide; this may be freed from the oily admixture by rubbing with methyl alcohol and subsequent recrystallisation from this solvent, from which it separates in glistening plates, m. p. 143—144° (Found: C, 58·5; H, 3·9; Cl, 20·2. $C_9H_7O_2Cl$ requires C, 59·2; H, 3·8; Cl, 19·5%).

2 : 4-*Dialdehydobenzoic Acid*, $CHO{\cdot}C_6H_3(CHO){\cdot}CO_2H$. — The chlorinated acid chloride (b. p. 184—186°/16 mm.; 47 g.) was boiled with chalk (50 g.) and water (300 c.c.) for 4 hours, precaution against access of air being taken by the use of a Bunsen valve attached to the top of the condenser. The product was cooled, acidified with concentrated hydrochloric acid, and, after remaining over-night, a gummy solid (A) was filtered off and the filtrate extracted three times with ether. The white solid obtained after drying and removing the ether separated from 50% acetic acid in nodules, m. p. 138—139°, and consisted of 2 : 4-dialdehydobenzoic acid. This was proved by mixing with a specimen of the dialdehydo-acid prepared as described on p. 2292, when there was no depression in m. p., and also by conversion into the characteristic dianilino-derivative, m. p. 208°. The gummy solid (A) mentioned above was again heated with chalk and water for 3 hours, and the filtered solution acidified. The crystalline precipitate so obtained was extracted with boiling water and filtered from gum when, on cooling, a crystalline mass of impure 4-*aldehydo*-1 : 2-*phthalide* was deposited and this separated from water, in which it was only sparingly soluble, in small plates, m. p. 159—160°, the yield being about 10% of theory (Found: C, 66·4; H, 3·6. $C_9H_6O_3$ requires C, 66·7; H, 3·7%). This substance is insoluble in sodium bicarbonate but dissolves on warming with sodium hydroxide. The *phenylhydrazone* is obtained by adding phenylhydrazine to the solution of the substance in dilute acetic acid and separates from alcohol in lemon-yellow needles, m. p. 171—172° (Found: N, 11·2. $C_{15}H_{12}O_2N_2$ requires N, 11·1%).

The Action of Alkali on 4-*Aldehydo*-1 : 2-*phthalide*.—When this phthalide (0·5 g.) was mixed with 2*N*-sodium hydroxide (5 c.c.) and warmed for about ½ minute on the steam-bath, complete solution took place. Addition of hydrochloric acid to the cooled solution precipitated a crystalline solid which, after drying in the vacuum desiccator, was found to be nearly pure 2-*hydroxy*-

* The decomposition of the methyl ester, $CHCl_2{\cdot}C_6H_3(CHCl_2){\cdot}CO_2Me$, into the syrupy 4-dichloromethyl-1 : 2-chlorophthalide is described on p. 2292.

methylterephthalic acid (see below) (Found : C, 55·8; H, 4·4. $C_9H_8O_5$ requires C, 55·1; H, 4·1%).

This acid was heated in the air-oven at 110° for an hour, extracted with cold sodium bicarbonate, filtered, and the filtrate acidified. The indefinite, crystalline powder so obtained melted at 279—280° and consisted of 4-*carboxy*-1 : 2-*phthalide*,

$$CO_2H{\cdot}C_6H_3{<}\begin{matrix}CH_2\\CO\end{matrix}{>}O$$

(Found : C, 60·6; H, 3·3. $C_9H_6O_4$ requires C, 60·7; H, 3·3%).

The lactone ring in this substance readily suffers hydrolysis when the substance is warmed with dilute sodium hydroxide, with the formation of the 2-hydroxymethylterephthalic acid, which apparently has no definite melting point but, on heating, gradually passes, with loss of water, into the lactone. Titration : 0·0884 required 8·9 c.c. of *N*/10-NaOH for neutralisation, whereas this amount of a dibasic acid, $C_9H_8O_5$, should neutralise 9·0 c.c.

2 : 4-*Di*(*dichloromethyl*)*benzoyl Chloride*, $CHCl_2{\cdot}C_6H_3(CHCl_2){\cdot}COCl$. —2 : 4-Dimethylbenzoyl chloride (p. 2284) was chlorinated in ultra-violet light at a temperature initially at 200° and rising to 220° in the apparatus described on p. 2289, until the amount of chlorine absorbed corresponded with the substitution of four atoms of hydrogen.

On twice fractionating, 60—70% of the product distilled at 192—193°/10 mm. as a nearly colourless oil which is not readily attacked by moist air (Found : Cl, 57·8. $C_9H_5OCl_5$ requires Cl, 57·9%). When the benzene solution of this chloride was mixed with aniline, the *anilide* of 2 : 4-di(dichloromethyl)benzoic acid was obtained which separated from alcohol in colourless needles, m. p. 159° (Found : Cl, 38·7; N, 3·9. $C_{15}H_{11}ONCl_4$ requires Cl, 39·1; N, 3·9%). The fact that this derivative appeared to be a single substance may be taken as evidence that the chloride consists essentially, if not entirely, of 2 : 4-di(dichloromethyl)benzoyl chloride.

2 : 4-*Di*(*dichloromethyl*)*benzoic Acid*, $CHCl_2{\cdot}C_6H_3(CHCl_2){\cdot}CO_2H$.—Owing to its stability to hydrolytic agents, some difficulty was experienced in converting the above acid chloride into the corresponding acid. Boiling with anhydrous formic acid decomposes the chloride fairly readily but also attacks the ω-chlorine atoms. Comparative experiments showed, however, that, if the temperature is not allowed to rise above 60°, hydrolysis is confined to the acid chloride group. The acid crystallises from the formic acid and is recrystallised from benzene–petroleum, separating in colourless needles, m. p. 159—160° (Found : Cl, 48·5. $C_9H_6O_2Cl_4$ requires Cl, 49·3%). The *methyl* ester, prepared by mixing the acid

chloride with methyl alcohol, is a colourless oil distilling at 186—188°/12 mm. (Found: Cl, 47·0. $C_{10}H_8O_2Cl_4$ requires Cl, 47·0%). This methyl ester is remarkably stable and may be distilled in small quantities at ordinary pressures with little decomposition, but when it is kept boiling, it gradually loses methyl chloride with the formation of 4-*dichloromethyl*-1 : 2-*chlorophthalide*,

$$CHCl_2 \cdot C_6H_3 \begin{<} CHCl \\ -CO- \end{>} O,$$

which distils at 297°/763 mm. and was not obtained crystalline (Found: Cl, 42·7. $C_9H_5O_2Cl_3$ requires Cl, 42·9%).

2 : 4-*Dialdehydobenzoic Acid*, $CHO \cdot C_6H_3(CHO) \cdot CO_2H$ (compare p. 2290).—The hydrolysis of 2 : 4-di(dichloromethyl)benzoyl chloride (30 g.) with precipitated chalk (40 g.) and water (300 c.c.) proceeds smoothly at the temperature of the boiling mixture if precautions are taken to exclude air during the process. After boiling for about 3 hours and until no oily drops of the chloride are left, the product is cooled, filtered, excess of hydrochloric acid added, and the whole left over-night. The crystalline solid is collected and the filtrate extracted several times with ether, as the aldehydo-acid is soluble in the acid solution. The solid so obtained is difficult to crystallise. It is very sparingly soluble in chloroform, benzene, or petroleum but readily so in acetone, alcohol or formic acid. It is also very soluble in water and does not crystallise on cooling. It may, however, be recrystallised from acetic acid (50%), separating in small nodules, m. p. 140—141°, the yield, calculated on the chloride employed, being about 70% (Found: C, 60·6; H, 3·5. $C_9H_6O_4$ requires C, 60·7; H, 3·3%). The *dianilino*-derivative is obtained when the alcoholic solution of the acid is warmed with aniline and separates from methyl alcohol in colourless needles, m. p. 208° (Found: C, 76·7; H, 5·0; N, 8·5. $C_{21}H_{16}O_2N_2$ requires C, 76·8; H, 4·9; N, 8·5%). This derivative is insoluble in sodium carbonate and dissolves in concentrated sulphuric acid to a yellow solution the colour of which is discharged on adding water.

Condensation with phenylhydrazine. When phenylhydrazine (2 mols.) is added to the solution of dialdehydobenzoic acid (1 mol.) in hot dilute glacial acetic acid, an orange oil is immediately precipitated which solidifies at once to a mass of yellow needles insoluble in sodium carbonate. After recrystallisation from alcohol, in which it is sparingly soluble, this *anhydro*-2 : 4-*dialdehydobenzoic acid diphenylhydrazone* is obtained in canary-yellow prisms, m. p. 264—266° (Found: C, 73·9; H, 4·6; N, 16·4. $C_{21}H_{16}ON_4$ requires C, 74·1; H, 4·7; N, 16·5%).

Condensation with p-*nitrophenylhydrazine.* When an alcoholic solution of dialdehydobenzoic acid was added to a hot dilute solu-

tion of *p*-nitrophenylhydrazine hydrochloride, a flocculent, orange precipitate separated which could not be recrystallised. It is insoluble in cold dilute sodium carbonate but dissolves with a dark claret colour on warming. It is immediately soluble in cold dilute sodium hydroxide. It seems probable that this substance is the p-*nitrophenylhydrazone* of 4-*aldehydo*-1 : 2-*hydroxyphthalide* and has the constitution $NO_2 \cdot C_6H_4 \cdot N_2H{:}CH \cdot C_6H_3 < \begin{matrix} CH(OH) \\ -CO- \end{matrix} > O$ (Found : C, 57·5; H, 3·8; N, 13·5. $C_{15}H_{11}O_5N_3$ requires C, 57·5; H, 3·5; N, 13·4%). This substance exhibits a curious behaviour in the melting-point tube, the reason for which is not clear. Having shrunk somewhat at 205—210°, it melts at 221—223°, solidifying almost at once and melting at 236—237°; after it has again solidified, its m. p. is about 180°. If *p*-nitrophenylhydrazine and dialdehydobenzoic acid, both dissolved in glacial acetic acid, are mixed, an orange powder separates which is only slowly hydrolysed by sodium hydroxide, melts at 235°, and appears to be an acetyl derivative of the above substance (Found : C, 57·5; H, 3·7; N, 11·8. $C_{17}H_{13}O_6N_3$ requires C, 57·5; H, 3·7; N, 11·8%). Lastly, if the condensation is performed in hot nitrobenzene solution, a substance is obtained in small, orange prisms, m. p. 295° (decomp.), which is evidently the dinitro-derivative of the anhydro-diphenylhydrazone,

$$NO_2 \cdot C_6H_4 \cdot N_2H{:}CH \cdot C_6H_3 < \begin{matrix} CH{:}N \\ | \\ CO \cdot N \cdot C_6H_4 \cdot NO_2 \end{matrix}$$

(Found : N, 19·2. $C_{21}H_{14}O_5N_6$ requires N, 19·5%).

Pentachloro-2 : 4-*dimethylbenzoyl Chlorides*, $CCl_3 \cdot C_6H_3(CHCl_2) \cdot COCl$ *and* $CHCl_2 \cdot C_6H_3(CCl_3) \cdot COCl$.—The introduction of five atoms of chlorine into 2 : 4-dimethylbenzoyl chloride (61 g.) is complete in about 3¼ hours under the influence of ultra-violet light, the temperature towards the end of the process being raised to 220° and the chlorination being conducted in the apparatus described on p. 2289. On distillation, no fractionation was accomplished, as the whole boiled between 188° and 192°/14 mm. Redistillation yielded a viscid, colourless liquid, b. p. 191—192°/14 mm., in a yield of 60—70% (Found : Cl, 62·7. $C_9H_4OCl_6$ requires Cl, 62·5%). As it was expected that this fraction would prove to be a mixture of the chlorides figured above, it was decided that the best evidence on this point would probably be obtained by the study of the behaviour of the supposed mixture on hydrolysis with chalk and water. The pentachlorinated acid chloride (120 g.) was boiled with excess of chalk and water in the usual manner for 12 hours, when, on cooling and acidifying, a crystalline mass separated immediately; this was filtered off and the filtrate (A) reserved for

further examination. The mass after two recrystallisations from acetic acid, in which it was only sparingly soluble in the cold, melted at 237° and consisted of 2-*aldehydoterephthalic acid*. The melting point was raised to 242° by dissolving in dilute sodium hydroxide and then adding excess of dilute hydrochloric acid; the clear solution, on standing over-night, had deposited long, glistening needles of the pure dibasic aldehydo-acid (Found: C, 55·9; H, 3·2. $C_9H_6O_5$ requires C, 55·7; H, 3·1%). Titration: 0·1636 required for neutralisation 16·8 c.c. of N/10-NaOH, whereas this amount of a dibasic acid, $C_9H_6O_5$, should neutralise 16·8 c.c.

The conversion of 2-aldehydoterephthalic acid into the corresponding alcohol and acid by the action of alkalis does not proceed so readily as in the case of 4-aldehydo-1 : 2-phthalide (p. 2279), since it was found necessary to boil with 25% sodium hydroxide to complete the decomposition. On acidifying the cold solution, a colloidal mass separated which was difficult to filter and, on dissolving the mass in boiling alcohol and allowing to cool slowly, a crystalline mass separated which melted at 280° and consisted of 4-*carboxy*-1 : 2-*phthalide*, since a mixed melting point with a specimen of this substance obtained as described on p. 2291 showed no depression.

Anhydro-2-*aldehydoterephthalic acid phenylhydrazone*,

$$CO_2H\cdot C_6H_3\begin{<}CH{:}N\\CO\cdot NPh\end{>},$$

is obtained by adding phenylhydrazine to the aqueous solution of the acid, and crystallises from alcohol in colourless clusters of prisms, m. p. 326—327°. This high melting point coupled with the absence of colour is in harmony with a derivative of terephthalic acid and the presence of the opiazone ring (Found: C, 68·1; H, 3·9; N, 10·4. $C_{15}H_{10}O_3N_2$ requires C, 67·7; H, 3·8; N, 10·5%). On titration, 0·0730 required 2·8 c.c. of N/10-NaOH for neutralisation, whereas this amount of a monobasic acid, $C_{15}H_{10}O_3N_2$, should neutralise 2·74 c.c.

2-*Aldehydoterephthalic Acid Oxime*, $CO_2H\cdot C_6H_3(CH{:}N\cdot OH)\cdot CO_2H$, *and the Imide of Trimellitic Acid*, $CO_2H\cdot C_6H_3\begin{<}CO\\CO\end{>}NH$.—When the aldehydo-acid (0·5 g.) is mixed with a concentrated aqueous solution of hydroxylamine hydrochloride (1 g.) and a little alcohol (3 c.c.), the crystals soon change into a thick precipitate of the oxime, which is difficult to recrystallise but separates from alcohol as a rather indefinitely crystalline powder (Found: C, 51·1; H, 3·6; N, 6·3. $C_9H_7O_5N$ requires C, 51·7; H, 3·3; N, 6·7%). On titration: 0·0839 required 8·2 c.c. of N/10-NaOH for neutral-

isation, whereas this amount of a dibasic acid, $C_9H_7O_5N$, should neutralise 8·03 c.c.

This oxime decomposes at about 136° with a slight puff and the melt almost immediately solidifies and melts again at about 242°. The substance so formed crystallises from water in needles, m. p. 248—249°, and has all the properties of the imide of trimellitic acid, a small specimen of which was prepared from trimellitic acid for comparison.

4-*Aldehydo*-1 : 2-*phthalic Acid*, $CHO{\cdot}C_6H_3(CO_2H){\cdot}CO_2H$.—The filtrate A (see above) from the 2-aldehydoterephthalic acid was extracted several times with ether and the ether removed, when a colourless, seemingly amorphous residue was obtained which contained 2 : 4-dialdehydobenzoic acid, trimellitic acid, and 4-aldehydophthalic acid. We were unsuccessful in our efforts to obtain the last acid in a state of purity, but it was easily identified by means of the phenylhydrazone. Addition of phenylhydrazine to a dilute acetic acid solution of the mixed acids soon precipitates a mixture of phenylhydrazones, on warming, which are partly soluble in dilute ammonia.

When the mixture was extracted with this reagent, anhydro-2 : 4-dialdehydobenzoic acid diphenylhydrazone (p. 2292) remained undissolved and was filtered off, and the weight of this showed that 2 : 4-dialdehydobenzoic acid must have been present to the extent of 25% of theory calculated on the original chlorinated chloride. The filtrate, on acidifying, deposited a gelatinous mass very difficult to filter and, when this was extracted with boiling water, the filtered extract deposited, on cooling, yellow nodules which melted at 118° and at the same time lost water and turned red. Analysis indicated that this substance is the *hydrate* of the *phenylhydrazone* of 4-*aldehydophthalic acid* (Found : C, 60·4; H, 4·7; N, 9·7. $C_{15}H_{12}O_4N_2,H_2O$ requires C, 59·6; H, 4·6; N, 9·3%). If this hydrate is exposed in a vacuum desiccator over sulphuric acid until the weight is constant, the mass melts at 174° with loss of water and is evidently the *phenylhydrazone* of 4-*aldehydophthalic acid* (Found : C, 63·4; H, 4·7; N, 9·7. $C_{15}H_{12}O_4N_2$ requires C, 63·4; H, 4·2; N, 9·9%).

When this substance is heated in the air-oven at 115°, it loses a molecule of water and is converted into the corresponding phthalic anhydride, an orange-red powder, m. p. 216—217°, which is not soluble in sodium carbonate (Found : C, 67·1; H, 3·7. $C_{15}H_{10}O_3N_2$ requires C, 67·7; H, 3·8%).

2 : 4-*Di*(*trichloromethyl*)*benzoyl Chloride*, $CCl_3{\cdot}C_6H_3(CCl_3){\cdot}COCl$, *and* 2 : 4-*Di*(*trichloromethyl*)*benzoic Acid*.—The above acid chloride is obtained from 2 : 4-dimethylbenzoyl chloride by introducing 6

chlorine atoms in the usual manner (compare p. 2289) and is a colourless oil, b. p. 192—196°/15 mm., which does not fume in moist air (Found : Cl, 65·2. $C_9H_3OCl_7$ requires Cl, 65·9%). Formic acid does not react with this acid chloride at all readily and, in order to being about hydrolysis and ensure that the decomposition was confined to the acid chloride group, it was found necessary to leave the mixture of the chloride and anhydrous formic acid for about 2 weeks with occasional shaking and warming to, but not above 60°. The solid was collected and recrystallised from petroleum, from which 2 : 4-*di(trichloromethyl)benzoic acid* separated in colourless needles, m. p. 170—171° (Found : Cl, 58·8. $C_9H_4O_2Cl_6$ requires Cl, 59·6%).

The *anilide*, obtained from the acid chloride by adding aniline to the solution in benzene, separates from alcohol, in which it is sparingly soluble, in colourless prisms, m. p. 202—203° (decomp.) (Found : Cl, 48·9; N, 3·4. $C_{15}H_9ONCl_6$ requires Cl, 49·3; N, 3·3%).

The *amide*, obtained by passing dry ammonia through the acid chloride dissolved in dry benzene, at the laboratory temperature, was collected, washed free from ammonium chloride, and crystallised from benzene, from which it separated in colourless needles which shrank at 165° and melted at 175—176° with evolution of hydrogen chloride (Found : Cl, 59·3. $C_9H_5ONCl_6$ requires Cl, 59·8%).

The *methyl* ester, obtained by boiling the chloride with methyl alcohol, is a thick, colourless liquid, b. p. about 210°/15 mm. Although odourless when cold, it becomes pungent and lachrymatory on warming (Found : Cl, 56·7. $C_{10}H_6O_2Cl_6$ requires Cl, 57·4%). The usual decomposition takes place on heating this ester to boiling and 4-*trichloromethyl*-1 : 2-*phthalyl chloride* is formed, a colourless liquid which distils at 186—187°/12 mm. and has a rather pleasant odour (Found : Cl, 55·6. $C_9H_3O_2Cl_5$ requires Cl, 55·4%). The fact that this substance does not fume in moist air and that it does not appear to be attacked by anhydrous formic acid to yield the corresponding substituted 4-trichloromethylphthalic acid, rather suggests the unsymmetrical formula. On the other hand, the addition of aniline to the solution in benzene causes the separation of a *dianilide* of the probable constitution $CCl_3{\cdot}C_6H_3(CO{\cdot}NHPh)_2$. This separates from alcohol, in which it is only sparingly soluble even on boiling, in minute colourless needles, m. p. 220° (Found : Cl, 24·8; N, 6·5. $C_{21}H_{15}O_2N_2Cl_3$ requires Cl, 24·7; N, 6·5%). It is curious that, whilst 2 : 4-di(trichloromethyl)benzoyl chloride is so resistant to hydrolysis by formic acid, it is readily decomposed by boiling with chalk and water under the usual conditions (p. 2290). On concentrating the solution of the calcium salt and

acidifying with a large excess of hydrochloric acid, trimellitic acid, m. p. 226—227°, is obtained in almost theoretical yield. On titration: 0·05 required 16·0 c.c. of 0·0444 *N*-$Ba(OH)_2$ for neutralisation, whereas this amount of a dibasic acid, $C_9H_6O_6$, should neutralise 16·06 c.c. *The calcium salt.* In one experiment, the concentrated product of the hydrolysis of the hexachlorobenzoyl chloride with chalk was mixed with insufficient hydrochloric acid, when, on standing, a highly characteristic calcium salt separated in feathery needles [Found: Ca, 22·4. $(C_9H_3O_6)_2Ca_3$ requires Ca, 22·4%]. This salt, which does not appear to have been described, is very sparingly soluble in boiling and almost insoluble in cold water.

The authors desire to thank the Chemical Society for a grant which has partly covered the cost of this investigation.

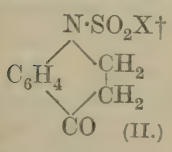
THE DYSON PERRINS LABORATORY,
OXFORD.

[*Received, July 20th,* 1925.]

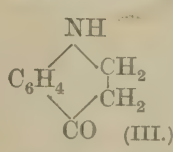
CCCXIV.—*Synthesis of Substituted* 4-*Keto*-1 : 2 : 3 : 4-*tetrahydroquinolines and an Attempt to Synthesise* 4-*Keto*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline.

By GEORGE ROGER CLEMO and WILLIAM HENRY PERKIN, jun.

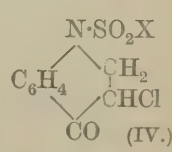
IN the first part of this research (J., 1924, **125**, 1608) it was shown that toluene-*p*-sulphonanilide condenses with β-chloropropionic acid to give the toluene-*p*-sulphonyl derivative of β-anilinopropionic acid, $NPh(SO_2{\cdot}C_6H_4Me){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$ (I) and that this, on treatment with phosphoric oxide, yields the toluene-*p*-sulphonyl derivative of 4-keto-1 : 2 : 3 : 4-tetrahydroquinoline * (II), from which the base itself (III) is obtained on hydrolysis. When, however, (I) is digested with phosphoryl chloride, the toluene-*p*-sulphonyl derivative of 3-chloro-4-ketotetrahydroquinoline (IV) is obtained as the result of combined ring closure and chlorination.



(II.)



(III.)



(IV.)

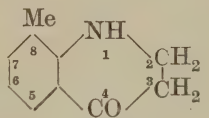
The formation of the chlorinated derivative (IV) and the fact that this is reduced to (III) with elimination of the toluene-*p*-sulphonyl

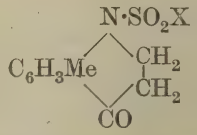
* Previously named 4-tetrahydroquinolone.

† The abbreviation $-SO_2X$ is used throughout for $-SO_2{\cdot}C_6H_4Me$.

group merely by heating with hydrochloric acid are very difficult to understand. It was mainly with the view of discovering some explanation for this remarkable decomposition that we decided to prepare other cases of a similar kind, and the result of this investigation is described in the present communication. In the first place, the three isomeric *toluene*-p-*sulphonyl*-β-*toluidinopropionic acids* of the type $C_6H_4Me{\cdot}N(SO_2X){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$ were prepared without difficulty from *o*-, *m*-, and *p*-toluidine by a process similar to that described in detail in the former communication. When the *o*-methyl derivative (Ia) was treated with phosphoryl chloride under the conditions previously used in the case of toluene-*p*-sulphonyl-β-anilinopropionic acid (I), a complex mixture was obtained from which a small amount of 4-*keto*-8-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (V; m. p. 92°) was isolated directly, together with a considerable quantity of a substance (VI, m. p. 147°), the analysis of which indicates that it is the toluene-*p*-sulphonyl derivative of (V).

(V.)





(VI.)

(VII.) (*o*)$C_6H_4Me{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}C_6H_4Me$(*o*)

The substance (VI) exhibits very remarkable properties. When it is boiled with a mixture of acetic and hydrochloric acids, it is hydrolysed to *o*-toluidine and β-*o*-toluidinopropionic acid,

$$C_6H_4Me{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H,$$

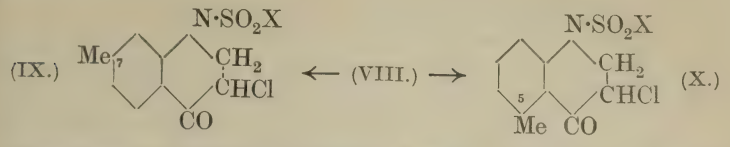
and when treated with concentrated sulphuric acid, (VI) yields β-o-*toluidinopropiono*-o-*toluidide* (VII, m. p. 126°), formed evidently by the condensation of the substances just mentioned, and the constitution of which is demonstrated by the fact that it is produced when the acid chloride of (Ia) is condensed with *o*-toluidine and the product hydrolysed with concentrated sulphuric acid.

If then (VI) represents the constitution of the substance of m. p. 147°, it is clear that, for some reason difficult to understand, scission of the ketotetrahydroquinoline ring must have taken place during the hydrolysis to the substances mentioned above.

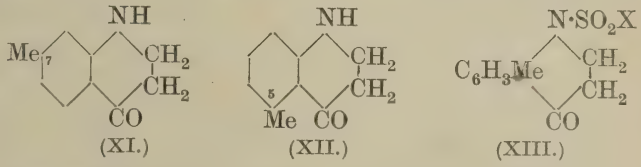
The investigation of the behaviour of *toluene*-p-*sulphonyl*-β-m-*toluidinopropionic acid* (VIII), m-$C_6H_4Me{\cdot}N(SO_2X){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, towards phosphoryl chloride has given results very different from those just decribed in the *o*-series.

In these circumstances, this acid behaves like toluene-*p*-sulphonyl-β-anilinopropionic acid (I; see p. 2297), yielding 3-chloro-derivatives, and, as might be expected, ring formation takes place in two

directions with the formation of the substances (IX) and (X) melting at 138° and 100°.



These isomeric *toluene*-p-*sulphonyl*-3-*chloro*-4-*keto*-5- and -7-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinolines* are both hydrolysed and reduced on boiling with hydrochloric acid, yielding 4-*keto*-5- and -7-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinolines* (XI) and (XII) melting at 109° and 105°.

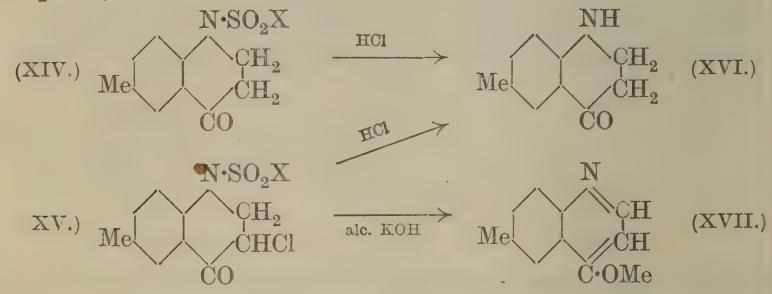


and these yield *toluene*-p-*sulphonyl* derivatives (XIII) melting at 98° and 136° respectively. With regard to the constitutions of these substances derived from *m*-toluidine, there is not sufficient evidence to enable us to assign definitely either formula (IX) or (X) to the toluene-*p*-sulphonyl-3-chloroketomethyltetrahydroquinoline of m. p. 138°. But it is significant that this substance is the main product of the ring closure, being present to the extent of 90% in the product of the action of phosphorus oxychloride on the substituted propionic acid.

In attempting to decide difficult questions of this kind, it must be remembered that ring closure in the benzene ring is, in fact, substitution and therefore the direction of ring closure should follow the rules which govern substitution. The tendency in the present case is probably to close the ring in the *p*-position to the methyl group, the *o*-closure being subsidiary. For this reason, the substance, m. p. 138°, produced in a yield of 90% is presumed to be (IX), in which case the isomeride, m. p. 100°, will be (X). The keto-methyltetrahydroquinoline, m. p. 109°, is then (XI) and the isomeride, m. p. 105°, is (XII). It may be mentioned that this view is borne out by other cases of a similar kind; thus, for example, *m*-toluidine is converted by the Skraup reaction mainly into 7-methylquinoline, and *m*-methoxyphenylhydrazine and acetone yield, by the Fischer synthesis, 6-methoxy-2-methylindole (compare Malkin and Robinson, this vol., p. 370).

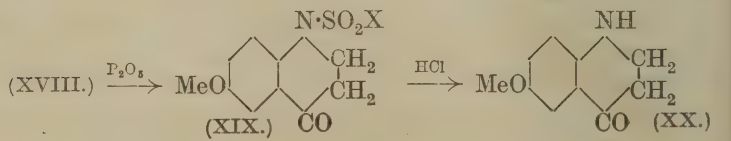
Toluene-p-*sulphonyl*-β-p-*toluidinopropionic acid* (compare p. 2304) was next prepared and its behaviour on treatment with phosphoric

oxide and oxychloride carefully investigated, when it was found that it yielded in the first case *toluene*-p-*sulphonyl*-4-*keto*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XIV), whereas it was converted by the oxychloride into the 3-*chloro*-derivative of this substance (XV). On boiling with dilute hydrochloric acid, both these substances yield 4-*keto*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XVI, m. p. 86°), and the chloro-derivative is converted by boiling with alcoholic potassium hydroxide into 4-*methoxy*-6-*methylquinoline* (XVII, m. p. 51°).



The behaviour of toluene-*p*-sulphonyl-β-*p*-toluidinopropionic acid during the course of this series of changes is therefore exactly similar to that of the corresponding β-anilino-derivative, described in detail in the earlier communication (*loc. cit.*, pp. 1609—1611).

The last series of experiments deals with the formation of methoxy- and ethoxy-derivatives of 4-keto-1 : 2 : 3 : 4-tetrahydroquinoline from *p*-anisidine and *p*-phenetidine, and was undertaken in order to determine whether the methoxy- or ethoxy-group has any considerable influence on the ease with which ketotetrahydroquinoline ring formation takes place. *Toluene*-p-*sulphonyl*-β-p-*anisidinopropionic acid* (XVIII), *p*-MeO·C_6H_4·N(SO_2X)·CH_2·CH_2·CO_2H, prepared from toluene-*p*-sulphonanisidide and β-chloropropionic acid in the usual manner, yielded on treatment with phosphoric oxide *toluene*-p-*sulphonyl*-6-*methoxy*-4-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XIX), from which 6-*methoxyketotetrahydroquinoline* (XX, m. p. 112°) was obtained by hydrolysis with acids.



That the methoxy-group has an influence on the mechanism of ring closure, different from that exerted by the methyl group, was shown by the behaviour of toluenesulphonylanisidinopropionic acid on

treatment with phosphorus oxychloride, since the product, instead of consisting entirely of *toluene*-p-*sulphonyl*-3-*chloro*-6-*methoxy*-4-*ketotetrahydroquinoline* (compare XV), contained only about 10% of this substance, the remainder consisting of the unchlorinated substance (XIX).

A similar series of observations was made in the case of *toluene*-p-*sulphonyl*-β-p-*phenetidinopropionic acid*,

$$EtO\cdot C_6H_4\cdot N(SO_2X)\cdot CH_2\cdot CH_2\cdot CO_2H\ ;$$

this substance, on treatment with phosphorus pentoxide, yields *toluene*-p-*sulphonyl*-6-*ethoxy*-4-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline*, from which the corresponding *ethoxyketotetrahydroquinoline* (m. p. 60°) is obtained on hydrolysis, whereas treatment with phosphorus oxychloride converts the acid into a mixture consisting mainly of the above toluene-*p*-sulphonyl derivative and containing only a small quantity of the corresponding 3-*chloro*-derivative.

It is interesting that these methoxy- and ethoxy-derivatives may be hydrolysed by hydrochloric acid to the corresponding hydroxy-derivatives; thus 6-methoxy-4-ketotetrahydroquinoline (XX) is converted by hydrochloric acid at 170° into 6-*hydroxy*-4-*ketotetrahydroquinoline*, which crystallises in deep yellow plates, m. p. 164°, and dissolves in sodium carbonate to a deep yellow solution.

The 3-*chloro*-derivatives produced by the action of phosphoryl chloride on toluene-*p*-sulphonyl-β-anilinopropionic acid and its substitution derivatives are readily distinguished from the corresponding unchlorinated substances by the fact that, whereas the former dissolve in strong sulphuric acid with intense violet colorations, hydrogen chloride being evolved, the solutions of the latter are colourless. A quantitative yield of the ketotetrahydroquinoline may be obtained from these colourless solutions, but in the case of the violet solutions the yield is generally only 80%, the remainder consisting of complex substances the nature of which has not been determined.

That these 3-chloro-derivatives should be formed at all under the conditions employed * is very difficult to understand, and that the chlorine atom in the 3-position should be so labile that it is replaced by hydrogen on treatment with hydrochloric acid is apparently without precedent. That the chlorine atom in the group

$$-CO\cdot CHCl\cdot CH_2\cdot N<$$

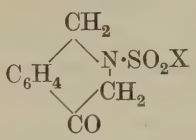
should be extremely reactive is in accordance with experience, since the bromine atom in the somewhat analogously constituted substance $CH_3\cdot CO\cdot CHBr\cdot CO_2Et$, for example, is readily reduced by cold

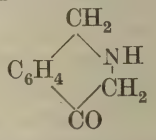
* That the formation of these chloro-derivatives is not due to the presence of pentachloride in the oxychloride was proved by experiments conducted with specially purified material.

hydriodic acid, but the only case in which it has been observed that a halogen atom is replaced by hydrogen by the action of hydrogen chloride appears to be that recently recorded by Ridgway and Robinson (J., 1924, **125**, 214), who showed that 8-ethoxy-2-phenylbenzopyrylium chloride is obtained from ethoxysalicylaldehyde and either acetophenone or ω-bromoacetophenone, $C_6H_5{\cdot}CO{\cdot}CH_2Br$, by treatment with hydrogen chloride.

During the course of this investigation, attempts were made to obtain derivatives of 4-ketotetrahydro*iso*quinoline corresponding to the 4-ketotetrahydroquinoline derivatives described in the preceding pages. *Toluene*-p-*sulphonbenzylamide* yielded, on condensation with sodium chloroacetate, *toluene*-p-*sulphonylbenzylaminoacetic acid* (m. p. 138°),

$$C_6H_5{\cdot}CH_2{\cdot}NH{\cdot}SO_2X + CH_2Cl{\cdot}CO_2Na \longrightarrow C_6H_5{\cdot}CH_2{\cdot}N(SO_2X){\cdot}CH_2{\cdot}CO_2H \longrightarrow$$





but all attempts to bring about the ring closure sketched above by the action of phosphoric oxide or phosphoryl chloride on the acid or of aluminium chloride on the acid chloride were unsuccessful.

Experimental.

Toluene-p-*sulphonyl*-β-o-*toluidinopropionic Acid*.* — Toluene-*p*-sulphon-*o*-toluidide (52·2 g.) was dissolved by warming in sodium hydroxide (100 c.c. of 8%), a solution of β-chloropropionic acid (22 g.) in sodium hydroxide (100 c.c. of 8%) added, and the mixture gently refluxed for 4 hours, during which some of the sulphon-*o*-toluidide separated as an oil. Water was added and the mixture cooled with stirring until the oily precipitate set to a granular, crystalline mass, which was filtered off, the filtrate acidified, and the colourless gum left over-night, when it had solidified. The solid dissolved completely in hot dilute sodium carbonate but, on cooling, some toluene-*p*-sulphon-*o*-toluidide, which is insoluble in cold sodium carbonate, separated. This was filtered off (total recovered = 27·5 g.), the filtrate acidified, the precipitate, which soon solidified, collected, washed with water, and dried on the steam-bath, when 28·5 g. of almost pure *toluene*-p-*sulphonyl*-β-o-*toluidinopropionic acid* resulted. This acid separated from a little benzene in colourless

* The same molecular quantities and procedure were employed in all the similar condensations described in this communication.

prisms, m. p. 127—128° (Found : C, 61·5; H, 5·7. $C_{17}H_{19}O_4NS$ requires C, 61·3; H, 5·7%).

Action of phosphoryl chloride. The acid (20 g.) was heated with phosphoryl chloride (60 c.c.) at 100° for 15 minutes, the excess of acid chloride removed under reduced pressure, and the gummy residue treated with ice and water and then warmed on the steam-bath for a few minutes. After cooling, the pale yellow aqueous solution was decanted from the gum (A) and made alkaline, when a small amount of a pale yellow solid separated which was collected, dried, and crystallised from light petroleum, from which yellow prisms of 4-*keto*-8-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (V), m. p. 92°, separated (Found : C, 74·7; H, 6·9. $C_{10}H_{11}ON$ requires C, 74·5; H, 6·8%). This substance is readily soluble in acids and also in alcohol or benzene to give solutions which have a green fluorescence. The gum (A) was warmed with dilute sodium carbonate, and after standing, the aqueous layer was decanted from the undissolved material and acidified, when a considerable quantity of toluenesulphonyltoluidinopropionic acid separated. The undissolved substance was crystallised from alcohol, when small prisms of the *toluene*-p-*sulphonyl* derivative of 4-*keto*-8-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (VI), m. p. 147—148°, separated (Found : C, 64·6; H, 5·4. $C_{17}H_{17}O_3NS$ requires C, 64·7; H, 5·4%). When this substance (1 g.) was dissolved in sulphuric acid (5 c.c.), the solution left over-night at the ordinary temperature, and poured on to ice and made slightly alkaline with sodium hydroxide, a colourless substance (about 0·4 g.) separated which crystallised from benzene–ligroin in colourless prisms, m. p. 126° and proved to be β-o-*toluidinopropiono*-o-*toluidide* (VII) (Found : C, 76·0; H, 7·6; N, 10·5. $C_{17}H_{20}ON_2$ requires C, 76·1; H, 7·5; N, 10·4%). The toluene-*p*-sulphonyl derivative of (VII) was synthesised in good yield by treating the acid chloride of toluene-*p*-sulphonyl-β-*o*-toluidinopropionic acid (Ia, from the acid and thionyl chloride) with *o*-toluidine. This substance is hydrolysed by cold concentrated sulphuric acid to give (VII), and boiling with hydrochloric acid converts it into *o*-toluidine and β-*o*-toluidinopropionic acid.

Toluene-p-*sulphonyl*-β-m-*toluidinopropionic Acid* (VIII).—This acid was prepared exactly as described in the case of the isomeric β-*o*-derivative; it dissolves readily in organic solvents and separates from benzene in stout, colourless prisms, m. p. 103° (Found : C, 61·4; H, 5·7. $C_{17}H_{19}O_4NS$ requires C, 61·3; H, 5·7%). The yield was 19 g., and 35 g. of the sulphonyl-*m*-toluidide were recovered.

Action of phosphoryl chloride. Toluene-*p*-sulphonyl-β-*m*-toluidinopropionic acid (VIII; 6 g.) was treated with phosphoryl chloride (20 c.c.) and the product worked up exactly as described in the

case of the corresponding *o*-acid. The substance insoluble in sodium carbonate was dissolved in a little methyl alcohol, when, on cooling, colourless prisms were quickly deposited which, after about 2 hours, were collected (filtrate A) and recrystallised from methyl alcohol, from which the substance separated in well-defined prisms, m. p. 138° (Found: Cl, 10·3. $C_{17}H_{16}O_3NClS$ requires Cl, 10·2%).

Toluene-p-*sulphonyl*-3-*chloro*-4-*keto*-7-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (IX) dissolves in sulphuric acid to an intense violet solution and when hydrolysed with a boiling mixture of acetic and hydrochloric acids (*loc. cit.*, p. 1616) gives an almost quantitative yield of 4-*keto*-7-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XI), which crystallises from benzene–ligroin in bright yellow leaflets, m. p. 109° (Found: C, 74·5; H, 6·8. $C_{10}H_{11}ON$ requires C, 74·5; H, 6·8%).

This substance is readily soluble in alcohol, giving a yellow solution with a pale green fluorescence, and, when treated with toluene-*p*-sulphonyl chloride, the *toluene*-p-*sulphonyl* derivative, *i.e.*, the unchlorinated analogue of (IX), is obtained; this separates from alcohol in rhombic prisms, m. p. 98°, and dissolves in sulphuric acid to an almost colourless solution (Found: N, 4·4. $C_{17}H_{17}O_3NS$ requires N, 4·4%).

The filtrate (A) contained the *toluene*-p-*sulphonyl* derivative of 3-*chloro*-4-*keto*-5-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (X; 0·29 g.) and, on standing, this gradually separated in colourless plates, which were recrystallised from ligroin and melted at 98—100° (Found: Cl, 10·3. $C_{17}H_{16}O_3NClS$ requires Cl, 10·1%). This substance gives the characteristic violet colour with sulphuric acid and is hydrolysed by acids to 4-*keto*-5-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XII), which crystallises from ligroin in long, yellow prisms, m. p. 104—105° (Found: C, 74·8; H, 7·0. $C_{10}H_{11}ON$ requires C, 74·5; N, 6·8%).

The *toluene*-p-*sulphonyl* derivative of this base crystallises from ligroin–benzene in long, almost colourless prisms, m. p. 136°, and dissolves in sulphuric acid without colour.

Toluene-p-*sulphonyl*-β-p-*toluidinopropionic Acid*.—This acid, prepared in the usual manner, separated from benzene in thin, colourless prisms, m. p. 116—117°. When it (6·6 g.) was treated with phosphoric oxide (5·6 g.) and xylene (50 c.c.) (compare *loc. cit.*, p. 1615), *toluene*-p-*sulphonyl*-4-*keto*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XIV) resulted; this separated from alcohol in colourless prisms, m. p. 136—137° (Found: N, 4·3. $C_{17}H_{17}O_3NS$ requires N, 4·4%).

This substance dissolves in sulphuric acid to an almost colourless solution and is hydrolysed by acids quantitatively to 4-*keto*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (see below).

When the β-*p*-acid, m. p. 116—117° (20 g.) was treated with

phosphoryl chloride (60 c.c.) in the usual manner (compare p. 2303), and the product insoluble in sodium carbonate crystallised from alcohol, *toluene*-p-*sulphonyl*-3-*chloro*-4-*keto*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XV) separated in well-defined, colourless, glistening prisms, m. p. 176—177° (Found : Cl, 10·2. $C_{17}H_{16}O_3NClS$ requires Cl, 10·2%).

This substance dissolves in sulphuric acid, with evolution of hydrogen chloride, to an intense purple solution and, on boiling with acetic and hydrochloric acids, undergoes hydrolysis, yielding 4-*keto*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XVI), which crystallises from benzene–ligroin in yellow plates, m. p. 85—86° (Found : C, 74·8; H, 6·8. $C_{10}H_{11}ON$ requires C, 74·5; H, 6·8%). This substance is readily soluble in dilute acids and in most organic solvents, giving the usual green fluorescent solutions. It yields a 3-*benzylidene* derivative, which crystallises from methyl alcohol in thin, yellow prisms, m. p. 224—225° (Found : C, 81·6; H, 5·9. $C_{17}H_{15}ON$ requires C, 81·9; H, 5·6%). This derivative readily combines with two atoms of bromine, and when the dibromide is refluxed with methyl-alcoholic potassium hydroxide, hydrogen bromide is removed and a *monobromo*-derivative is obtained which crystallises from alcohol in stout, colourless prisms, m. p. 194—195°, and gradually dissolves in dilute alkali (Found : C, 62·4; H, 4·4; Br, 24·1. $C_{17}H_{14}ONBr$ requires C, 62·2; H, 4·3; N, 24·4%).

4-*Methoxy*-6-*methylquinoline* (XVII).—The chloro-derivative (20 g.) was refluxed for 16 hours with methyl-alcoholic potassium hydroxide (75 c.c. of 20%), the alcohol removed, water added, the oily base extracted with benzene, dried over potassium hydroxide, and fractionated, when 8 g. passed over at 185°/18 mm. and crystallised; it separated from ligroin (b. p. 60—80°) in needles, m. p. 51° (Found : C, 76·0; H, 6·4. $C_{11}H_{11}ON$ requires C, 76·3; H, 6·3%).

Toluene-p-*sulphonyl*-β-p-*anisidinopropionic Acid* (XVIII).—This acid was prepared from toluene-*p*-sulphonanisidide and β-chloropropionic acid and crystallised from benzene in small, colourless prisms, m. p. 81—82° (Found : C, 58·4; H, 5·5. $C_{17}H_{19}O_5NS$ requires C, 58·5; H, 5·4%). Treated in xylene solution with phosphoric oxide under the conditions described in detail in the previous communication (*loc. cit.*, p. 1616), it yielded *toluene* p-*sulphonyl*-6-*methoxy*-4-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XIX), which separated from alcohol in colourless prisms, m. p. 124—125° (Found : N, 4·3. $C_{17}H_{17}O_4NS$ requires N, 4·2%). This substance dissolves in sulphuric acid to a colourless solution and is hydrolysed by acids to 6-*methoxy*-4-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline* (XX; see below).

When the acid (XVIII) (20 g.) was digested with phosphoryl chloride under the usual conditions, and the product insoluble in sodium carbonate boiled with a little methyl alcohol and filtered from about 0·5 g. of insoluble material (Y), the filtrate deposited 8·5 g. of a substance which, on recrystallisation, separated in colourless prisms, m. p. 115—120°. Analysis indicated that this substance was a mixture of about 90% of the substance (XIX) with about 10% of the corresponding 3-chloro-derivative (compare p. 2300).

When this mixture was hydrolysed with acids, it gave a large yield of 6-*methoxy*-4-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline*, which crystallised from benzene–ligroin in bright yellow prisms, m. p. 112° (Found : C, 67·8; H, 6·3. $C_{10}H_{11}O_2N$ requires C, 67·8; H, 6·2%).

This substance is a strong base and dissolves readily in most organic solvents to give deep yellow solutions exhibiting a green fluorescence. The substance (Y), sparingly soluble in alcohol, separates from acetic acid in colourless prisms, m. p. 235° (Found : C, 58·3; H, 4·2; N, 4·2; Cl, 9·8. $C_{17}H_{16}O_3NClS$ requires C, 58·4; H, 4·2; N, 4·0; Cl, 9·2%). This analysis suggests that this substance may be *toluene*-p-*sulphonyl*-3-*chloro*-6-*methoxydihydroquinoline*, but the amount available was too small for further investigation. It dissolves in sulphuric acid to a colourless solution with an intense pale blue fluorescence.

Toluene-p-*sulphonyl*-β-p-*phenetidinopropionic Acid* (compare XVIII).—Prepared from toluene-*p*-sulphonphenetidide and β-chloropropionic acid, this acid crystallises best from 75% methyl alcohol, in colourless, well-defined prisms, m. p. 97° (Found : C, 59·8; H, 6·0. $C_{18}H_{21}O_5NS$ requires C, 59·5; H, 5·8%). On treatment with phosphoric oxide, it yields a small amount of *toluene*-p-*sulphonyl*-6-*ethoxy*-4-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline*, which separates from methyl alcohol in rectangular prisms, m. p. 114—115° (Found : C, 62·2; H, 5·5. $C_{18}H_{19}O_4NS$ requires C, 62·6; H, 5·5%). This substance gives a colourless solution in sulphuric acid. When the phenetidinopropionic acid was treated with phosphoryl chloride, it yielded a small amount of a substance, m. p. 232°, sparingly soluble in alcohol which clearly corresponds with the substance (Y) described above but was not further examined. The alcoholic filtrate deposited a crystalline substance melting approximately at 100° which was again a mixture consisting mainly of toluene-*p*-sulphonyl-6-ethoxy-4-keto-1 : 2 : 3 : 4 - tetrahydroquinoline and containing a small proportion of the corresponding 3-*chloro*-derivative. When this mixture was hydrolysed by hydrochloric acid, it yielded 6-*ethoxy*-4-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline*, which separated from benzene–ligroin in canary-yellow leaflets, m. p. 60° (Found : C, 69·0; H, 6·9. $C_{11}H_{13}O_2N$ requires C, 69·1; H,

6·8%). This strongly basic substance dissolves in most organic solvents to yellow solutions exhibiting a green fluorescence.

6-*Hydroxy*-4-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline*.—This substance was obtained when the corresponding methoxy-derivative (XX; 4·5 g.) was heated with concentrated hydrochloric acid (30 c.c.) in a sealed tube at 160—170° for 6 hours. On cooling, the hydrochloride separated as a pale brown, crystalline mass, which was collected, stirred with cold concentrated sodium acetate solution, and the yellow base (3·5 g.) crystallised from xylene, from which it separated in deep yellow plates, m. p. 163—164° (Found : C, 66·6; H, 5·6. $C_9H_9O_2N$ requires C, 66·3; H, 5·5%). This substance is sparingly soluble in benzene, but dissolves readily in alcohol and in aqueous sodium carbonate to deep yellow solutions.

Toluene-p-*sulphonylbenzylaminoacetic Acid*.—Toluene-*p*-sulphonbenzylamide (J., 1905, **87**, 159; 31·2 g.) was dissolved in hot sodium hydroxide (90 c.c. of 8%), a solution of chloroacetic acid (13 g.) in sodium hydroxide (90 c.c. of 8%) added, and the whole refluxed gently for 48 hours. The mixture was then well cooled, acidified with hydrochloric acid, the colourless solid collected, washed with water, extracted with aqueous sodium carbonate, and the undissolved toluene-*p*-sulphonbenzylamide (26·5 g.) filtered off. The acid (5·5 g.) obtained on acidifying the filtrate crystallised from ligroin in long, hair-like prisms, m. p. 137—138° (Found : C, 59·8; H, 5·3. $C_{16}H_{17}O_4NS$ requires C, 60·2; H, 5·5%). When the solution of this acid in alcohol was saturated with dry hydrogen chloride and refluxed for 24 hours, the *ethyl* ester was obtained; it separated from ligroin in rectangular plates, m. p. 51° (Found : N, 4·0. $C_{18}H_{21}O_4NS$ requires N, 4·0%).

The authors are indebted to the British Dyestuffs Corporation for permission to publish the results of this investigation.

THE DYSON PERRINS LABORATORY,
OXFORD.

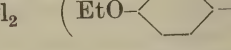
[*Received, July 20th,* 1925.]

CCCXV.—*Interactions of Tellurium Tetrachloride and Aryl Alkyl Ethers. Part I.*

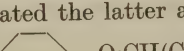
By GILBERT T. MORGAN and HARRY DUGALD KEITH DREW.

WITH purely aliphatic ethers tellurium tetrachloride combines additively to form unstable hygroscopic compounds of the type $Et_2O,TeCl_4$, but with mixed ethers containing aryl and alkyl radicals substitution takes place with elimination of hydrogen chloride.

These observations were first made by Rust (*Ber.*, 1897, **30**, 2829), who condensed phenetole with tellurium tetrachloride, obtaining a compound which separated in yellow needles melting at 185° to which he ascribed formula I. This result was supported by the preparation and analysis of a series of derivatives and homologues.

(I.)  (II.) 

A few years later (*Annalen*, 1901, **315**, 9), Rohrbaech, in repeating the phenetole condensation, obtained Rust's halogenated compound and reduced it with zinc to a halogen-free substance, yellow plates of m. p. 64°, to which he gave formula II. The assumption that in this condensation tellurium entered the aromatic nucleus was, however, challenged by Lederer (*Ber.*, 1915, **48**, 2049; 1916, **49**, 2532), who prepared both di-*p*-phenetyl telluride (formula II) and its di-*o*-isomeride from tellurium dibromide and the corresponding magnesium aryl halides, $EtO{\cdot}C_6H_4{\cdot}MgI$.

These diaryl tellurides, the constitution of which was not in doubt, differed from the Rust-Rohrbaech product and accordingly Lederer designated the latter as an ethylidene compound with the constitution  (III). He also repeated the Rust-Rohrbaech preparation and obtained the orange-red telluride melting at 64°, thus confirming the previous result. Moreover, he generalised his conclusion by a more complete investigation of the corresponding di-*o*-, *m*-, and *p*-anisyl tellurides, which all differed from the product of the Rust-Rohrbaech preparations with anisole and tellurium tetrachloride.

These seemingly exhaustive investigations appeared to show beyond doubt that tellurium did not enter the aromatic nucleus in the Rust condensation and that isomeric compounds were produced with tellurium attached to the side chain.

However, in preparing the Rust-Rohrbaech product in order to test its possible bactericidal properties we used chloroform as a convenient solvent and obtained a large yield of a substance corresponding in properties with Rust's yellow dichloride. This compound on reduction with alkali metabisulphite was completely transformed to the expected orange-red substance. On testing the solubility of this product in water, it was noticed that the crystals did not melt in the boiling solvent, in which they remained insoluble. Examination of fusibility revealed a melting point of 107° and not 64° as given by Rohrbaech and by Lederer. This compound (IV) and the chloride (V), which gave it by reduction,

were therefore analysed and found to possess respectively the following molecular formulæ,

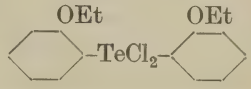
(IV.) $(C_2H_5\cdot O\cdot C_6H_4)_2Te_2$ m. p. 107°. $(C_2H_5\cdot O\cdot C_6H_4)TeCl_3$ (V.) m. p. 183°.

these constitutions being confirmed by the whole of the physical and chemical characteristics of the substances.

Rust and Rohrbaech's formulations for these two substances as diaryl telluride and diaryl tellurium dichloride respectively, although supported by many concordant analyses, are entirely erroneous.

In the course of the present investigation the true dichloride has been prepared and identified. On being heated with more phenetole, the phenetyltellurium trichloride (m. p. 183°) passes into a colourless bisphenetyltellurium dichloride melting at 108°. This compound in all probability is *bis*-p-*phenetyltelluridichloride* (VI), since it melts at 108°, whereas the bis-*o*-phenetyltelluridichloride (VII) prepared by Lederer through the Grignard reaction melts at 163—164°.

(VI.) 

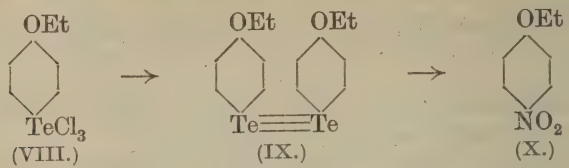
(VII.) 

It seems probable that Rust, Rohrbaech, and Lederer were dealing with mixtures of the di- and tri-chlorides and in the case of the last two investigators they also had mixtures of the reduction products of these chloro-derivatives. But it is nevertheless remarkable that the analytical data should agree with those demanded by an incorrect formulation and that the melting point of a compound described as a dichloride, $(EtO\cdot C_6H_4)_2TeCl_2$, should agree with that of the substance now shown to be the trichloride, $EtO\cdot C_6H_4\cdot TeCl_3$.

With our present knowledge of the organic chemistry of tellurium the colour of the products is a useful guide to constitution. Telluridichlorides are invariably colourless and their reduction products are yellowish-white to pale yellow. Telluritrichlorides, on the contrary, are often yellow and their reduction products are intensely coloured (Morgan and Drew, this vol., p. 531).

As further evidence of constitution it was noticed that when the bis-*p*-phenetyl ditelluride was covered with cold concentrated nitric acid and the mixture allowed to evaporate, *p*-nitrophenetole (X) separated, the tellurium being displaced by a nitro-group. This evidence is opposed to Lederer's conclusion as to the attachment of tellurium to the side chain and indicates that the metalloid has entered the para-position with respect to ethoxyl,

thus confirming the following formulæ for p-*phenetyltelluritrichloride* (VIII) and *bis*-p-*phenetyl ditelluride* (IX).



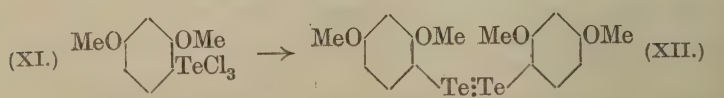
Lederer's work is defective in another respect. He reduced the Rust-Rohrbaech product from anisole and tellurium tetrachloride, obtaining red needles (m. p. 50°) to which, like Rohrbaech, he assigned a diaryl telluride formula but with tellurium in the side chain, $(C_6H_5{\cdot}O{\cdot}CH_2)_2Te$. On warming this substance with methyl iodide, he obtained a product yielding a picrate alleged to be anisyldimethyltelluronium picrate, $C_6H_2(NO_2)_3{\cdot}O{\cdot}Te(CH_3)_2{\cdot}CH_2{\cdot}O{\cdot}C_6H_5$, one anisyl residue having been eliminated during methylation. The methylation product would accordingly be the iodide, $C_6H_5{\cdot}O{\cdot}CH_2{\cdot}Te(CH_3)_2I$. But actually we find that the supposed "dianisyl telluride," which is in reality bis-*p*-anisyl ditelluride, undergoes on warming with methyl iodide a smooth decomposition into molecular proportions of iodo-derivatives,

$$R{\cdot}Te{:}TeR + 3MeI = RTeMe_2I + RTeMeI_2,$$

where R is the anisyl residue.

The products are the less soluble p-*anisyldimethyltelluri-iodide*, which gave Lederer his picrate, and the more soluble p-*anisylmethyltelluridi-iodide*, which is easily reduced to p-*anisyl methyl telluride*. Lederer evidently overlooked the more soluble product, and his hypothesis, based on the assumption of an elimination of one of the *p*-anisyl radicals, falls to the ground.

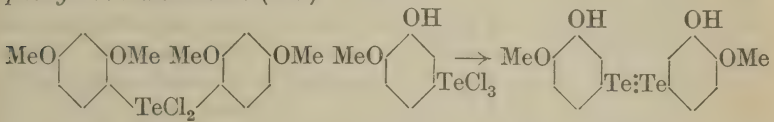
In order to test our conclusions as to the nature of the tellurium tetrachloride condensation with mixed ethers the case of the dimethyl ether of resorcinol was examined. The product was found to be the yellow 1 : 3-*dimethoxyphenyl*-4-*telluritrichloride* (XI), which on reduction furnished the orange-brown *bis*-1 : 3-*dimethoxyphenyl* 4 : 4-*ditelluride* (XII).



When the condensation was forced by heating the reaction mixture with excess of tellurium tetrachloride the tellurium content fell instead of increasing by further substitution in the nucleus; the

product was the colourless *bis*-1 : 3-*dimethoxyphenyl*-4-*telluridichloride* (XIII), while the excess of tetrachloride remained unchanged.

Guaiacol behaves similarly although less smoothly, yielding a 2-*hydroxy*-1-*methoxyphenyl*-4-*telluritrichloride* (XIV), isolated with difficulty but reducing to an orange-brown *bis*-2-*hydroxy*-1-*methoxyphenyl* 4 : 4-*ditelluride* (XV).



(XIII.) (XIV.) (XV.)

Experimental.

Condensation of Tellurium Tetrachloride with Phenetole.

When a mixture of 12 g. of tellurium tetrachloride, 17 g. (3 mols.) of phenetole, and 75 c.c. of dry chloroform was heated under reflux, with exclusion of moist air, during 2 hours, hydrogen chloride was evolved and the solid dissolved. The solution deposited during heating a copious precipitate of glistening, yellow flakes consisting of practically pure p-*phenetyltelluritrichloride* (VIII), which was removed after one day, washed with a little cold chloroform, and dried (yield, 14·5 g. or 92%). This substance was moderately soluble in hot chloroform or benzene to yellow solutions and was readily soluble in cold ethyl alcohol to a solution which was colourless owing to hydrolysis. On warming with aqueous potash the trichloride developed the odour of phenetole. It melted to a red liquid at 182—183° and further crystallisation from dry chloroform resulted in no alteration (Found : Cl, 30·25. $C_8H_9OCl_3Te$ requires Cl, 30·0%).

Bis-p-*phenetyl Ditelluride* (Formula IX).—The foregoing trichloride (6 g.), reduced at 0° with 11·3 g. (3 mols.) of potassium metabisulphite and 50 c.c. of water, gave crude *bis*-p-*phenetyl ditelluride*, in almost quantitative yield, as an orange powder which crystallised from petroleum (b. p. 80—100°) in fluffy masses of brilliant, orange-red needles or golden-orange plates, melting at 107—108° to a deep red liquid. It was readily soluble in cold benzene or chloroform, but much less soluble in light petroleum or ethyl alcohol, and was insoluble in water. Its solutions in organic solvents were red. It was unaffected by boiling aqueous ammonia, but was decomposed by methyl iodide (compare the corresponding *p*-anisyl compound, p. 2314) [Found : C, 38·75; H, 3·4; Te, 51·3; *M*, cryoscopic in benzene, 473 (c = 1·89), 481 (c = 2·92). $C_{16}H_{18}O_2Te_2$ requires C, 38·6; H, 3·6; Te, 51·3%; *M*, 497].

Although the ditelluride crystallised well from ethyl or methyl alcohol, the product from these solvents was invariably slightly high in carbon content (found: C, 39·25, 39·1; H, 3·7, 3·7), indicating the presence of an impurity which was not completely eliminated by subsequent crystallisation from petroleum. It was noticed, also, that solutions of the ditelluride, when unduly exposed to the air, tended to deposit an amorphous oxide which was again reduced to the ditelluride by the action of aqueous alkali bisulphites. When bis-*p*-phenetyl ditelluride was covered with cold concentrated nitric acid and the solution allowed to evaporate in an open basin, large, colourless spears of *p*-nitrophenetole separated. This substance melted at 60—61° and did not depress the melting point of an authentic specimen of *p*-nitrophenetole (Kahlbaum).

Bis-p-*phenetyltelluridichloride* (Formula VI).—When *p*-phenetyltelluritrichloride was heated with four times its weight of phenetole during 6 hours on an oil-bath at 180—190°, hydrogen chloride was evolved and the addition of petroleum then caused the deposition of *bis*-p-*phenetyltelluridichloride*, which was purified by crystallisation from methyl alcohol. The dichloride formed colourless, glistening, prismatic needles, melting at 108° to a colourless, transparent liquid. In this substance the chlorine was very firmly attached, being only slowly liberated (along with phenetole) even by boiling aqueous potash (Found: C, 43·3; H, 4·0; Cl, 16·1. $C_{16}H_{18}O_2Cl_2Te$ requires C, 43·6; H, 4·1; Cl, 16·1%).

Condensation of Tellurium Tetrachloride with Resorcinol Dimethyl Ether.

Tellurium tetrachloride (2·9 g.), resorcinol dimethyl ether (1·5 g.; 1 mol.), and dry chloroform (30 c.c.), when heated on the water-bath during 2 hours, evolved hydrogen chloride and formed a deep brownish-yellow solution. After removal of the chloroform, a syrup remained which crystallised when it was stirred with a little cold carbon tetrachloride, this solvent poured off, and a little chloroform added. The yellow, crystalline powder (2·7 g.) consisted of crude 1 : 3-*dimethoxyphenyl*-4-*telluritrichloride* (XI), which was purified by crystallisation from dry chloroform. The trichloride formed silky, primrose-yellow, prismatic needles or transparent, golden-yellow prisms, melting at 155—156° to a yellow liquid which at once became red. On warming with aqueous potash the compound evolved resorcinol dimethyl ether (Found: Cl, 28·8. $C_8H_9O_2Cl_3Te$ requires Cl, 28·7%).

When the proportion of resorcinol dimethyl ether in the foregoing condensation was increased to 2 mols. (4·2 g. of tellurium tetrachloride, 4·2 g. of resorcinol dimethyl ether, and 10 c.c. of dry

chloroform heated on the water-bath during 11 hours), the solid product (4·9 g.) was a mixture of the yellow trichloride and colourless *bis*-1 : 3-*dimethoxyphenyl*-4-*telluridichloride* (XIII). Similarly, when 2 mols. of tellurium tetrachloride and 1 mol. of resorcinol dimethyl ether were employed and a higher temperature was obtained by diminishing the proportion of solvent (6·7 g. of tellurium tetrachloride, 1·8 g. of resorcinol dimethyl ether, and 12 c.c. of dry chloroform heated on the water-bath for 3 hours), a second atom of tellurium was not introduced into the aromatic nucleus; but, instead, a portion of the tellurium tetrachloride remained unchanged and the product consisted of the dichloride admixed with a proportion of trichloride. Reduction with an excess of aqueous potassium metabisulphite led to the destruction of the trichloride, leaving the dichloride unchanged. The latter was extracted from the black reduction product by means of boiling ethyl alcohol, from which it separated on cooling. *Bis*-1 : 3-*dimethoxyphenyl*-4-*telluridichloride* crystallised from alcohol in colourless, pearly flakes which melted without apparent decomposition at 204—205°. It was resistant to the reducing action of aqueous alkali bisulphite, but was decomposed by hot aqueous potash with liberation of resorcinol dimethyl ether (Found : Cl, 14·9. $C_{16}H_{18}O_4Cl_2Te$ requires Cl, 15·0%).

In the above condensations of tellurium tetrachloride with phenetole and with resorcinol dimethyl ether, respectively, the fact that a telluritrichloride is practically the sole product when an excess of the aromatic ether is used in the case of phenetole, but not in that of resorcinol dimethyl ether, seems to be due mainly to the comparative insolubility in chloroform of the telluritrichloride of phenetole. This product is thrown out of solution as formed and in the presence of chloroform is only slowly changed to a dichloride by the further action of another molecule of phenetole.

Bis-1 : 3-*dimethoxyphenyl* 4 : 4-*Ditelluride* (XII).—1 : 3-Dimethoxyphenyl-4-telluritrichloride (1·2 g.), reduced with 2·1 g. of potassium metabisulphite and 10 c.c. of water, was quantitatively transformed to the ditelluride, which was extracted with ether and purified by crystallisation from benzene, petroleum (b. p. 80—100°), or ethyl alcohol. *Bis*-1 : 3-*dimethoxyphenyl* 4 : 4-*ditelluride* separated in orange-brown needles or prisms, a specimen from benzene melting at 134—135° to a deep red liquid. It was insoluble in water, but moderately soluble in ether or ligroin to orange-red solutions. It was unaffected by aqueous alkalis, but gave an intense reddish-purple coloration with cold concentrated sulphuric acid [Found : C, 36·1; H, 3·6 (specimen from benzene) :

C, 37·0; H, 3·5 (specimen from alcohol). $C_{16}H_{18}O_4Te_2$ requires C, 36·3; H, 3·4%].

Condensation of Tellurium Tetrachloride with Guaiacol.

Tellurium tetrachloride (1 mol.) was mixed with guaiacol (2 mols.) and dry chloroform (5 c.c. per g. of tellurium tetrachloride). Hydrogen chloride was evolved and a deep yellowish-green solution was formed on heating during 2½ hours on a water-bath. This solution, concentrated to a syrup in a vacuum desiccator, partly solidified after extraction of unchanged guaiacol by means of petroleum. The greenish-yellow solid was separated by boiling with dry chloroform or benzene into an amorphous, insoluble, mustard-yellow powder decomposing near 180° (not identified) and 2-*hydroxy*-1-*methoxyphenyl*-4-*telluritrichloride* (XIV), which separated from dry chloroform in transparent, deep yellow prisms, m. p. 157—159° (decomp.). This substance, which was readily hydrolysed by moist air when in solution, was not obtained in a pure condition (Found: Cl, 28·9. $C_7H_7O_2Cl_3Te$ requires Cl, 29·8%).

When reduced with aqueous potassium metabisulphite at 0°, the telluritrichloride was transformed to *bis*-2-*hydroxy*-1-*methoxyphenyl* 4 : 4-*ditelluride* (XV), which was extracted by means of ether and subsequently purified by crystallisation from dry benzene. The ditelluride formed orange-brown, prismatic needles, slowly darkening above 114° and melting finally at 117—118° with liberation of tellurium. It was sparingly soluble in petroleum, but moderately soluble in benzene, chloroform, or ether, giving red solutions. Boiling ethyl alcohol caused its decomposition. It was insoluble in water, but dissolved in aqueous caustic soda or sodium carbonate (although not in aqueous sodium bicarbonate) to yellowish-orange solutions of the sodium salt, from which the ditelluride was reprecipitated on addition of mineral acids (Found: C, 33·8; H, 2·95. $C_{14}H_{14}O_4Te_2$ requires C, 33·55; H, 2·8%). Addition of chloroacetic acid to a solution of the ditelluride in aqueous caustic soda caused the precipitation of purplish-blue flakes of a substance which soon decomposed when removed from the liquid but was more stable in the form of its red solution in dilute aqueous caustic soda.

Action of Methyl Iodide on Bis-p-*anisyl Ditelluride.*—The deep red-brown solution of 5 g. of the pure ditelluride (m. p. 56—58°) in 78 g. of pure methyl iodide was heated under reflux on a water-bath for ½ hour, when a microcrystalline, salmon precipitate (4·6 g.) of p-*anisyldimethyltelluri-iodide*, $CH_3{\cdot}O{\cdot}C_6H_4{\cdot}Te(CH_3)_2I$, was thrown down (see equation, p. 2310). This substance melted at 170—172° and was almost insoluble in acetone, benzene, and other organic

solvents, but was hydrolysed by boiling alcohol. It was not reduced by aqueous alkali bisulphites. When warmed with aqueous sodium picrate containing free picric acid, it was decomposed giving two picric acid compounds: (1) Lederer's picrate,

$$CH_3{\cdot}O{\cdot}C_6H_4{\cdot}Te(CH_3)_2{\cdot}O{\cdot}C_6H_2(NO_2)_3,$$

forming bright yellow needles from alcohol or water, m. p. 126—127°; and (2) a substance forming pale yellow, glistening plates from alcohol, which decomposed with effervescence to a transparent, yellow liquid at 176° after changing slowly from about 160°. This substance was probably an additive compound of picric acid and *p*-anisyl methyl telluride, the latter being formed from the above iodide by loss of methyl iodide on heating.

The methyl iodide mother-liquor from the foregoing telluri-iodide contained only p-*anisylmethyltelluridi-iodide*,

$$CH_3{\cdot}O{\cdot}C_6H_4{\cdot}Te(CH_3)I_2$$

(4·7 g.), a red, crystalline substance melting at 109° and soluble in organic solvents (Found: I, 50·1. $C_8H_{10}OI_2Te$ requires I, 50·4%). This substance was readily reduced on shaking with aqueous potassium metabisulphite in presence of ether, with formation of p-*anisyl methyl telluride*, a yellow oil of nauseating odour. Part of the di-iodide, however, was re-transformed to bis-*p*-anisyl ditelluride by partial reduction followed by intramolecular loss of methyl iodide. The reactions occurring may be represented as follows:—

(1) $MeO{\cdot}C_6H_4{\cdot}TeMeI_2 \xrightarrow{2H} 2HI + MeO{\cdot}C_6H_4{\cdot}TeMe.$

(2) $2MeO{\cdot}C_6H_4{\cdot}TeMeI_2 \xrightarrow{2H}$
$2HI + MeO{\cdot}C_6H_4{\cdot}TeMeI{\cdot}TeMeI{\cdot}C_6H_4{\cdot}OMe \longrightarrow 2HI + 2MeI +$
$MeO{\cdot}C_6H_4{\cdot}Te{:}Te{\cdot}C_6H_4{\cdot}OMe.$

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CCCXVI.—*A New Aspect of the Photochemical Union of Hydrogen and Chlorine.*

By Ronald G. W. Norrish.

Part I. *A General Theory of the Change.*

On account of its great interest to the student of chemical kinetics, the photochemical reaction between hydrogen and chlorine has received a very large amount of attention during the past hundred years. In spite of this, no theory which describes the mechanism completely has yet been given, and, indeed, few reactions have proved more difficult to interpret. The results which have accumulated from recent work, however, throw a new light upon the problem, and taken together, enable deductions to be drawn which greatly simplify it. In the present paper, a theory of the process is presented which is claimed completely to describe the mechanism, uniting such diverse phenomena as the effects of desiccation and the induction period in one general explanation. It will be shown that harmony between the various phases of the reaction is attained if we accept the view that the primary photochemical reaction—the dissociation of the chlorine molecule into atoms—takes place at the surface of the vessel, and that a quantitative expression on the basis of the existing theory of Nernst can be built up which is in agreement with the experimental findings of Chapman and his co-workers.

One aspect of the reaction, namely, its extreme deviation from Einstein's law of photochemical equivalence (Bodenstein, *Z. Elektrochem.*, 1913, **19**, 836), has found a simple explanation in the chain theory of Nernst ("Grundlagen der neuen Wärmesatzes," Halle, 1918, p. 133). The primary action of the light is considered to be a dissociation of the chlorine molecules in accordance with simple quantum relations. Subsequent action takes place in the manner shown in the following equations (*a*) and (*b*), both of which may be shown thermodynamically to represent reactions of large affinity.

$$Cl + H_2 = HCl + H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$
$$H + Cl_2 = HCl + Cl \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

It will be seen that the absorption of one light quantum, by its generation of two chlorine atoms, can thus originate two chains of reactions which are propagated indefinitely throughout the gaseous mixture by the alternate repetition of reactions (*a*) and (*b*), giving rise to a very large number of hydrogen chloride molecules.

The Rôle of Water in the Reaction.—Before we can apply the chain theory of Nernst to explain the complicated relationships found to

hold good by M. C. C. Chapman, in her quantitative study of the reaction (J., 1923, **123**, 3062), it will be necessary to consider in some detail the bearing of the recent work of Coehn and Jung upon the effects of desiccation on the velocity of hydrogen chloride formation, and an important deduction to which this gives rise. The subject was originally opened by Baker (J., 1894, **65**, 612), who showed that combination of the two gases under extremely dry conditions proceeded only very slowly in sunlight, instead of by explosion. Bodenstein and Dux (*Z. physikal. Chem.*, 1913, **85**, 297), on the other hand, showed definitely that desiccation down to a water vapour pressure of 10^{-3} mm. of mercury produced no effect upon the velocity of combination of the two gases. More recently, Coehn and Jung (*ibid.*, 1924, **110**, 705) have been able to extend the limit of desiccation down to a water vapour pressure of 10^{-7} mm., at which point they found the formation of hydrogen chloride to be suspended. From their results and those of Bodenstein and Dux it is evident that the velocity of hydrogen chloride formation is independent of water vapour pressure, when the latter is increased upwards beyond the limit of 10^{-4} mm. but that below this pressure it gradually falls off to zero. No explanation of these important facts was put forward by Coehn and Jung, but the suggestion is here advanced that they become readily explainable if we draw the deduction that *the primary photochemical reaction requires water as a catalyst and takes place only at the walls of the vessel.*

Modern views of adsorption have led us to the belief that surface affinity is in general neutralised by a single layer of adsorbed molecules, and over their whole range of experimentation we may consider that Bodenstein and Dux were dealing with a glass surface completely saturated with water molecules and therefore offering a reaction surface of constant properties. At water vapour pressures below 10^{-4} mm., with preliminary baking out under a vacuum, this surface layer of molecules is unsaturated, until, at 10^{-7} mm., the surface is practically dry, and the formation of hydrogen chloride is suspended.*

This hypothesis is rendered more probable by some simple calculations relative to Coehn and Jung's conditions of experimentation. Their cylindrical reaction bulbs were 10 c.c. in volume, corresponding to a surface area of about 30 sq. cm. The radius of the water molecule being taken as 2×10^{-8} cm., the number required completely to cover the surface is about 2×10^{16}. The number of water mole-

* This explanation may well apply to other cases of the suspension of reaction between gases on extreme drying, which may be regarded as due, not to the "ultra-dryness" of the gases, but to the removal of the catalytically active water film from the walls of the vessel.

cules filling the bulb at 10^{-4} mm. is about $3{\cdot}5 \times 10^{13}$—about 600 times too small to cover the surface—whilst at 10^{-7} mm. the number is 6×10^{-5} times too small. From Coehn and Jung's account of their work it would appear that their experimental bulbs were left for some time in communication with the source of water vapour pressure before sealing off, so that, while in the former case there would probably be time for a distillation of water vapour to occur sufficient to cover the dried surface of the vessel, there would in a like period only be time to cover one-thousandth of the surface at the lower pressure, and probably even less, since the walls of the communicating tubes also have to be saturated. We may therefore suppose that somewhere in the neighbourhood of 10^{-3} or 10^{-4} mm. of water vapour pressure the moisture film at the surface of the reaction vessel ceases to be saturated, and the velocity of hydrogen chloride formation, in accordance with our hypothesis, begins to fall off at this point.

These considerations lead us to the conclusion that dissociation of the chlorine molecule, which is a necessary preliminary to the starting of the Nernst reaction chains referred to above, must occur through the intermediate formation of a loose complex of chlorine and water at the glass surface. It is possible that a hydrate of the form $\begin{matrix}H\\H\end{matrix}\!>\!O\!<\!\begin{matrix}Cl\\Cl\end{matrix}$ exists in the gaseous phase, and such a compound may also be formed at the surface, but under the latter condition it may well be so weakened structurally by the influence of the surface forces as to render photochemical dissociation of the compound possible at the surface, while impossible in the gaseous phase. Thus we may write :

$$\begin{matrix}H\\H\end{matrix}\!>\!O\!<\!\begin{matrix}Cl\\Cl\end{matrix} = H_2O + 2Cl.$$

As an alternative view, we may suppose that, under the combined influence of the force fields of the glass surface and the water molecules, the chlorine molecule receives an induced polarity which renders it the more easily dissociable (see Norrish, J., 1923, **123**, 3006).* Coehn and Jung (*loc. cit.*) have found, moreover, that when the photochemical reaction between hydrogen and chlorine is promoted by ultra-violet light, extreme desiccation has no influence

* In any case there can be no doubt that chlorine adsorbed at the water film covering a glass surface is much more reactive than gaseous chlorine. This has recently been experimentally demonstrated by the present author in conjunction with Mr. Glyn-Jones for the case of the reaction between ethylene and chlorine. This reaction occurs rapidly at the glass surface, and not at all in the gaseous phase, or on a non-polar and dry paraffin wax surface. Details of this work will be published later.

on the velocity of the reaction, and we may assume that the larger energy quantum here concerned is capable of dissociating the dry gaseous chlorine molecules, so that the primary photochemical reaction can occur in this case in the gaseous phase also.

Confining our attention, however, to the action of visible radiation only, we see that the Nernst reaction centres must first originate at the water film of the surface, with chlorine atoms produced there, and may then travel outward into the gaseous phase, each centre being alternately represented by a hydrogen and a chlorine atom as a result of the endless repetition of reactions (*a*) and (*b*) above. A centre of reaction once started will persist until it meets either another centre or encounters the wall of the vessel. In the former case, the atoms of the two centres will combine with each other; in the latter, reaction will occur between the atoms of the centre and the dissociated chlorine atoms at the surface, or with the water at the surface. Since the partial pressure of reaction centres in the system must be extremely minute, encounters of these with the wall of the vessel will be much more frequent than encounters with one another, so that mutual neutralisation may be assumed negligible compared with neutralisation at the surface.

It would thus appear a reasonable deduction that the primary photochemical reaction—the quantised dissociation of the chlorine molecule—occurs as a surface reaction catalysed by water, and that the reaction centre so started (consisting alternately of atomic hydrogen and chlorine) moves outward into the gaseous phase, being destroyed only when it meets the walls of the vessel, or—much more rarely—another centre.

The Induction Period.

The deductions as to the nature of the primary photochemical reaction set forth above suggest a simple explanation of the induction period on the basis of a surface poisoning by foreign substances. Any impurity capable of combining preferentially with the moisture film at the surface of the reaction vessel should act as a poison to the primary photochemical reaction and inhibit the formation of hydrogen chloride. Burgess and Chapman have shown that small traces of ammonia, or impurities producing ammonia, can give rise to artificial induction periods. Arguing from the strong affinity of ammonia for water, there can be little difficulty in ascribing its action to preferential combination with the moisture film. In Part II of this paper the kinetics of the induction period are studied in more detail, and a quantitative research is described which strongly confirms the present hypothesis.

The Anticatalytic Effect of Oxygen.

It was established independently both by Chapman and McMahon (J., 1909, **95**, 135, 959) and by Bodenstein and Dux (*loc. cit*). that the rate of combination of hydrogen and chlorine is inversely proportional to the oxygen concentration. Thus, keeping the partial pressure of hydrogen and chlorine constant, we may write :

$$d[\mathrm{HCl}]/dt = k/[\mathrm{O_2}].$$

Norrish and Rideal (this vol., p. 787) have confirmed the suggestion of Chapman that at the same time the hydrogen and oxygen gradually unite to form water under the photosensitive action of the chlorine. The relationship found to hold between the velocity of water formation and the concentrations of chlorine and oxygen may be expressed by the formula :

$$d[\mathrm{H_2O}]/dt = k'[\mathrm{Cl_2}][\mathrm{O_2}].$$

This reaction receives a simple explanation by assuming that chlorine molecules throughout the gaseous phase, rendered active by the absorption of a light quantum, can activate oxygen by the transfer of intra-atomic energy on collision. We may assume that a similar deactivation is possible at the surface, and in order to explain completely the anticatalytic effect of hydrogen discovered by M. C. C. Chapman it is necessary to assume that oxygen can deactivate the surface molecules only when it collides simultaneously with a hydrogen molecule. Thus water may be formed by photosensitisation throughout the gaseous phase and at the surface, but it is only the latter process that is to be regarded as connected with the anticatalytic effects of oxygen and hydrogen.

The Kinetics of the Hydrogen–Chlorine Reaction.

These ideas will now be applied to the development of a theoretical expression, connecting the rate of formation of hydrogen chloride with the partial pressures of hydrogen, chlorine, and oxygen in the system, which is in complete agreement with the experimental findings of D. L. Chapman and his school (see especially M. C. C. Chapman, J., 1923, **123**, 3078).

Let the gaseous concentration of the components be represented by square brackets enclosing the corresponding formulæ, and constants by K, k, etc. It will be assumed that the chlorine may be adsorbed at the surface of the water film, the fraction, ϕ, of the total area covered being small compared with unity. Under the influence of the light, the adsorbed chlorine gradually reacts with hydrogen to form reaction centres; when a stationary state has been reached,

$$k_1[\mathrm{Cl_2}] = k_2[\mathrm{H_2}]\phi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Let N be at any moment the number of molecules of photochemically activated chlorine present per sq. cm. of surface. Not all of these are to be regarded as capable of starting reaction chains, but only a small fraction which under a favourable combination of circumstances may be considered as completely dissociated.* All the active chlorine molecules at the surface, however, may be deactivated when simultaneously struck by a hydrogen and an oxygen molecule, with the resulting photosensitive formation of water, and also by thermal degradation of their energy, the number deactivated by these two processes being regarded as large compared with those which react with hydrogen. Equating the rates of activation and deactivation at the surface, we have, therefore, when a stationary state has been reached,

$$k_3 I\phi = k_4 N[H_2][O_2] + k_5 N \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where I represents the intensity of illumination.

Combining equations (1) and (2) and collecting constants,

$$N = K_1 I[Cl_2]/[H_2]([H_2][O_2] + k) \quad . \quad . \quad . \quad . \quad (3)$$

Let s and v be the total surface and the volume of the vessel, and n the number of reaction centres present at any moment per c.c. of the reacting system. The rate of production of centres is, according to hypothesis, proportional to the number of contacts between surface active chlorine molecules and the bombarding hydrogen molecules. Hence

$$dn/dt = k_6 sN[H_2]/v \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The reaction centres are destroyed on again meeting the walls of the vessel, the constituent atoms reacting there with the adsorbed atomic chlorine or the water. Hence, the much smaller number of centres destroyed in the gaseous phase being neglected,

$$-dn/dt = k_7 ns/v \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where s/v is the surface available per unit of volume. Equating equations (4) and (5) for a stationary state, and combining with equation (3), we obtain

$$n = K_2 I[Cl_2]/[H_2][O_2] + k \quad . \quad . \quad . \quad . \quad (6)$$

Now, for a given reaction centre, let t_1 be the average time required for a hydrogen molecule to react with the chlorine atom, and t_2 the time required for a chlorine molecule to react with the hydrogen atom.

* For instance, the active molecule may pass through a series of vibrations, only one phase of which is equivalent to dissociation from the point of view of the bombarding hydrogen molecules.

Then: $t_1 = a/[H_2]$ and $t_2 = b/[Cl_2]$,

where a and b are constants.

In $(t_1 + t_2)$ seconds two molecules of hydrogen chloride are formed per centre, and the process then repeats itself. From n centres, therefore, $2n/(t_1 + t_2)$ molecules of hydrogen chloride are produced per second,

or $$d[HCl]/dt = 2n/(a/[H_2] + b/[Cl_2]) \quad . \quad . \quad . \quad . \quad (7)$$

Combining equations (6) and (7), we obtain finally:

$$d[HCl]/dt = KI[H_2][Cl_2]^2/([H_2][O_2] + k)(a[Cl_2] + b[H_2]) \quad . \quad (8)$$

This expression is completely satisfactory as a general formula for the description of the results of M. C. C. Chapman (*loc. cit.*), if a and b are regarded as comparable in magnitude, and k as small compared with the product $[H_2][O_2]$, except when $[H_2]$ is very small.

The predictions of this expression may be summarised in a manner parallel to the summary of experimental results given by M. C. C. Chapman (*loc. cit.*, p. 3078), and it will be seen on comparison that there is close agreement between experiment and theory:—

(1) No term for the total pressure of the reacting gases is involved in the expression, and $d[HCl]/dt$ is therefore independent of the total pressure of the gas.

(2) If $[H_2]$ and $[O_2]$ be kept constant,

(*a*) $d[HCl]/dt \propto [Cl_2]$ when $[H_2]$ is small.
(*b*) $d[HCl]/dt \propto [Cl_2]^{(2-x)}$ when $[H_2] \fallingdotseq [Cl_2]$, x being less than unity.
(*c*) $d[HCl]/dt \propto [Cl_2]^2$ when $[Cl_2]$ is small.

(3) If $[Cl_2]$ and $[O_2]$ be kept constant,

(*a*) $d[HCl]/dt \propto [H_2]$ when $[H_2]$ is small.
(*b*) $d[HCl]/dt \propto 1/[H_2]^{1-x}$ when $[Cl_2] \fallingdotseq [H_2]$, x being comparable with unity.
(*c*) $d[HCl]/dt \propto 1/[H_2]^{1-x}$ when $[Cl_2]$ is small, x being small compared with unity.

(4) If $[H_2]$ and $[Cl_2]$ be kept constant,

(*a*) $d[HCl]/dt \propto 1/[O_2]$
except
(*b*) $d[HCl]/dt = k$ when $[H_2]$ is very small.

Summary.

Recent work by Coehn and Jung has shown that while the rate of combination of hydrogen and chlorine in visible radiation is uninfluenced by desiccation down to a water vapour pressure of 10^{-4} mm., it approaches zero between 10^{-4} and 10^{-7} mm. In

explanation, it is here suggested that the primary photochemical reaction—the dissociation of the chlorine molecule into atoms—occurs only at the water film covering the walls of the vessel and that its rate is uninfluenced while the surface layer of water is saturated, but decreases when this is only partly saturated at low water vapour pressures. The resulting "Nernst chains" must extend outward into the gaseous phase, and be destroyed on again meeting the surface. This hypothesis leads to an expression in full agreement with Chapman's quantitative researches.

Part II. *An Experimental Study of the Mechanism and Nature of the Period of Induction.*

It was early observed by Bunsen and Roscoe in their researches on the photochemical union of hydrogen and chlorine (*Phil. Trans.*, 1857, **147**, 381) that the combination of these two gases is preceded by a period of quiescence during which no reaction occurs. This phenomenon, to which they applied the name "photochemical induction," remained a puzzle to early experimenters, until Burgess and Chapman, in a now classical paper (J., 1906, **89**, 1899), showed it to be due to the inhibiting action of small quantities of ammoniacal impurities present in the water of the insolation vessel.

The explanation suggested by Chapman and McMahon (J., 1909, **95**, 1717; 1910, **97**, 847) was based on the supposed production of small quantities of nitrogen trichloride, by the chlorine from the ammoniacal impurities, and the subsequent oxidation of the hydrogen chloride as it was formed, presumably according to the equation $NCl_3 + 3HCl = NH_3 + 3Cl_2$. Such an explanation suffers from the defect that it puts no limit to the period of induction, for the ammoniacal impurity is repeatedly regenerated, and should therefore *continuously* suspend the formation of hydrogen chloride. It is also extremely difficult to conceive of a minute trace of foreign substance *completely* inhibiting a homogeneous gaseous reaction by secondary reaction with one of the products; at best we should expect a decrease in the velocity of hydrogen chloride formation dependent on the concentration of the nitrogen trichloride in the system.

The later suggestion of Chapman and McMahon (*loc. cit.*), that the activated chlorine molecules are used up in sensitising the reduction of the inhibitor by hydrogen, has been confirmed by Norrish and Rideal (this vol., p. 787) for the case of the anticatalytic effect of oxygen and may well apply in the case of some of the other impurities, *e.g.*, nitrogen peroxide; but it is overstrained if we attempt to explain the complete inhibitory effect of ammonia by its means. The two series of phenomena are quite distinct and cannot

be grouped together. On the one hand, the additions of relatively large quantities of oxygen merely *decrease* the velocity of hydrogen chloride formation in inverse ratio to its concentration, whilst on the other, much smaller quantities of ammonia (as will be evident from the data of this paper) *completely inhibit* the hydrogen–chlorine reaction for a period of time proportional to the quantity of ammonia added. The subsequent hydrogen–chlorine reaction which sets in suddenly at the end of the induction period rapidly reaches a maximum velocity which from the observed Draper effects bears no relation to the original ammonia concentration.

These difficulties led the present author to reject the mechanism suggested by Chapman and McMahon as insufficient, and particularly since the conclusions arrived at in Part I of this paper indicate an alternative explanation which is more in accord with experimental fact. If the deduction that the primary photochemical dissociation of the chlorine occurs at the water film covering the walls of the vessel is accepted, we have a very simple means of explaining the induction period as due to a surface poisoning by preferential adsorption of ammonia derived from these impurities. We may suppose that the ammonia covers the surface, and removes from the sphere of action the water essential to the chlorine dissociation, and that the poison must first be removed by reaction with the illuminated chlorine before the surface can be rendered active.

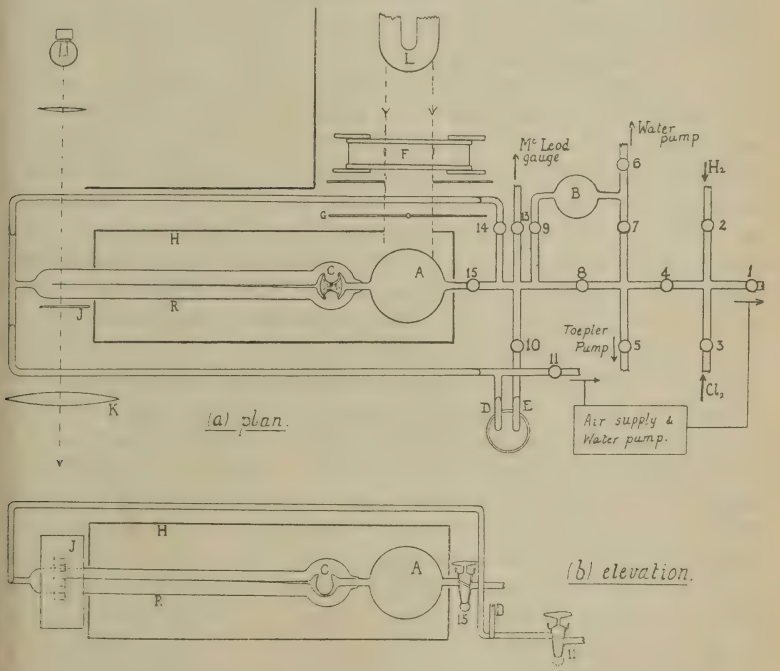
In order to test the likelihood of this view it was necessary to obtain quantitative data relating the induction period to the amount of ammonia, chlorine, and hydrogen in the system, and to the surface extent, and to this end the experimental researches described below were undertaken. The measurements which have been obtained have proved accurately reproducible, and consistent with the hypothesis of surface poisoning advanced above.

In devising an apparatus capable of dealing rapidly and accurately with small quantities of ammonia, it was deemed necessary to dispense with water, present in the insolation vessels of most workers, as absorbent for the hydrogen chloride. As it was only necessary for the present purpose to observe the instant of onset of the hydrogen–chlorine reaction and not its velocity, advantage was taken of the Draper effect or sudden increase of pressure of the gaseous system due to the heat given out when the hydrogen and chlorine start reacting. Another difficulty proved the admission of a small and accurately known amount of ammonia gas to the system. This was eventually solved by making use of the molecular compound of silver chloride and ammonia, $2AgCl,3NH_3$ (Bodländer, *Z. physikal. Chem.*, 1892, **9**, 730), which exerts a known and manageable dissociation pressure of ammonia at the ordinary temperature (Isam-

bert, *Compt. rend.*, 1868, **66**, 1529) and could be used as a source of definite small doses of ammonia.

The apparatus used may be described by reference to Fig. 1. The reaction vessel consisted of a glass bulb (A), of capacity 185 c.c. and diameter 7·0 cm. for most of the experiments described. The reaction chamber was connected on the one hand to the gas supplies and vacuum pumps *via* tap (15), and on the other to an enclosed Bourdon gauge (C). This gauge, which is efficient either as a direct-recording instrument for small pressure changes of from

FIG. 1*a* and 1*b*.



1 mm. to 50 mm., or as a " null " instrument for recording pressures up to one atmosphere, is made by blowing a thin glass bulb of about 7 cm. capacity, attaching a style of glass about 20 cm. long, and then heating in the flame and sucking in one side to the shape shown at (C) in Figs. 1a and 1b. Variation of pressure inside the gauge caused movement of the style, the shadow of which was focussed on a translucent scale (J) and observed through a magnifying glass or telescope (K). The gauge was sealed inside an outer vessel (R), the internal pressure of which could be varied by allowing air to enter or leave by tap (11), and measured by means of the mercury

manometer (D). By equalising the pressures outside and inside the gauge, the pressure of the chlorine gas in A could be measured without the direct use of mercury manometers, which are corroded by the gas. The gauge also proved an accurate and efficient indicator of the small pressure changes due to the Draper effect used as the basis of these measurements.

The source of illumination was a quartz mercury vapour lamp (L) carrying a direct constant current of 3·5 amp. from a 220-volt supply, and placed 20 cm. from the front surface of the bulb (A). The light from the lamp traversed a water cooler (F), with parallel plate-glass sides, which removed the infra-red and ultra-violet rays, and could be screened from the reaction vessel by means of the opaque screen (G). The reaction bulb also and the greater part of the gauge were enclosed in a tin canister as a screen from adventitious radiation. The amount of light falling on the bulb was limited by a hole, 4 cm. in diameter, in the side of this canister, and a stop of the same diameter placed in front of the water cooler. These conditions were kept constant throughout the whole of the comparative measurements to be described. The technique of the chlorine and hydrogen manipulation was essentially the same as that described by Norrish and Rideal (this vol., p. 787), except that the pressure of the former gas was measured by means of the Bourdon gauge as already described. The chlorine was obtained from a cylinder of liquid chlorine, was purified from any hydrogen chloride or ammonia by passage through water, and dried by means of fused calcium chloride. Independent analysis showed that the gas delivered by the cylinder contained no detectable oxygen. The hydrogen was obtained from a cylinder of the compressed gas, and carefully purified from oxygen by passage and repassage over red-hot palladised copper; it was stored in an aspirator over strong soda solution and dried by calcium chloride before admission to the apparatus. The silver chloride–ammonia compound was enclosed in the blackened bulb, B, which was isolated by stopcocks (7) and (9) from the rest of the apparatus and kept filled with pure hydrogen. Definite doses of ammonia could be expanded from B into A by means of the hydrogen gas as carrier. The other connexions of the apparatus are sufficiently evident from the diagram and need no description.

After a preliminary evacuation of the reaction vessel (A) and gauge envelope (R) by means of the water-pumps, the former was exhausted by the Toepler pump until the pressure of the contained air indicated by the McLeod gauge was not greater than 0·05 mm. The pump was then shut off from the apparatus and tap (8) closed. " Ammoniated hydrogen " was then expanded from B into A *via* taps (9) and

(15) until the required pressure, indicated by the mercury manometer (E), was attained. Simultaneously air was allowed to enter the envelope (R) until the same pressure was reached. The bulb (B) was then refilled with hydrogen for later use, by way of taps (2), (4), and (7). After re-evacuation of the connecting tubes, hydrogen to the required pressure registered by the manometer E was expanded into the reaction vessel with the simultaneous admission of air to the gauge envelope, as before. Finally, after the connecting tubes had been again evacuated and "washed out" and the manometer E isolated by tap (10), the chlorine was expanded from its container into the reaction vessel, its pressure being measured by adjusting the style of the gauge to zero on the scale by simultaneously admitting air to the envelope (R).

During this period of gaseous manipulation the lamp had been allowed to reach a steady state of running, the screen (G) being in position. The bulb containing hydrogen, chlorine, and ammonia at known pressures was now exposed to radiation from the lamp, the instant of removal of the screen being noted. The image of the style of the gauge on the illuminated scale was now watched, and readings of its position were made at short intervals. In general, during the induction period the gauge indicator steadily remained at zero, and when this terminated, the onset of the hydrogen–chlorine reaction was marked by a very sudden movement of the style along the scale, as a result of the pressure increase due to the emission of heat by the combining gases. The time from the first instant of illumination to the moment when the first movement of the gauge indicator was observed was noted as the induction period. The increase of pressure rapidly reached a maximum, and continued with a very slow fall as long as the gases were illuminated. If the screen were replaced, the pointer immediately moved back to zero, and on re-illumination the Draper effect *immediately* manifested itself; showing that there is no tendency for the induction period to reappear. A typical graph of these pressure changes is given in Fig. 2 and it will be seen that they are sharp enough to enable the induction period to be obtained to a high degree of accuracy. Its termination could usually be marked to a second or so by means of a stop-watch.

No control of the temperature was included in the apparatus, and was purposely omitted, since water cooling tends to minimise the Draper effect, which is required to be as large as possible for the accuracy of these measurements. The loss of accuracy by this omission is probably very small, since it is well known that photochemical reactions are in general little affected by small changes of temperature. In any case, the temperature of the room rarely

varied from 17° by more than one degree. The temperature of the bulb B was always recorded and from a knowledge of the dissociation pressure of the silver chloride–ammonia compound, and the amount of hydrogen expanded from B into A, the quantity of ammonia carried into the reaction chamber could be calculated.

In Tables I, II, and III are given the results of measurement of the induction period under standardised conditions.

(*a*) Varying the ammonia pressure and keeping the pressure of hydrogen and chlorine constant.

(*b*) Varying the hydrogen pressure, and keeping that of the chlorine and ammonia constant.

(*c*) Varying the chlorine pressure and keeping that of the ammonia constant.*

FIG. 2.

Pressure changes on illumination, showing induction period.

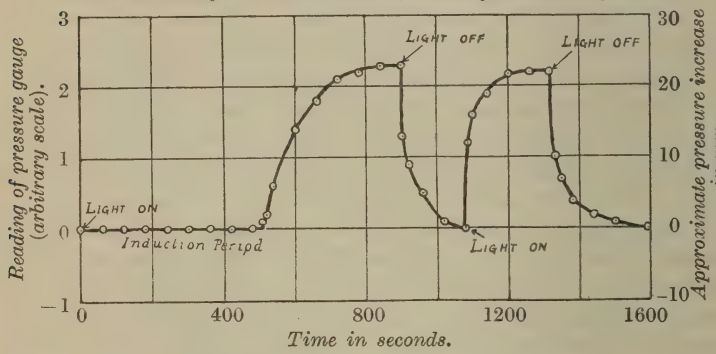


TABLE I.

Variation of Induction Period with Pressure of Ammonia.

Total pressure of hydrogen 160—170 mm.
Total pressure of chlorine 470—490 mm.

x = pressure of "ammoniated hydrogen" admitted to reaction vessel in mm. of Hg; p, the pressure of ammonia in mm. of Hg, $= x \times 0{\cdot}0116$ (correct to 0·05 mm. of Hg); T = induction period in seconds.

x.	p.	T.	$(T/p) \times 10^{-2}$.	x.	p.	T.	$(T/p) \times 10^{-2}$.
0	0	0	—	102	1·30	510	3·9
11	0·15	60	4·0	124	1·45	570	3·9
13	0·15	55	3·7	149	1·75	710	4·1
30	0·35	145	4·1	166	1·95	925	4·7
30	0·35	135	3·9	167	1·95	820	4·2
55	0·65	250	3·8				Mean 4·02
82	0·95	375	4·0				

* It was unnecessary to keep the hydrogen pressure constant in this series, since, as will be seen from Table II, its variation has no effect upon the period of induction.

TABLE II.

Effect of Hydrogen Pressure on the Induction Period.

Pressure of ammonia 0·35 mm. of Hg.
Pressure of chlorine 195—210 mm. of Hg.

Pressure of hydrogen in mm. of Hg	75	117	149	200	300	410	466
Induction period in seconds	180	188	170	165	180	170	180

TABLE III.

Pressure of ammonia 0·35 mm. of Hg.

Pressure of chlorine in mm. of Hg.	Induction period in seconds. Obs.	Calc. T = 90 $(1 + 200/P)$.	Pressure in chlorine in mm. of Hg.	Induction period in seconds. Obs.	Calc. T = 90 $(1 + 200/P)$.
46	540	481	235	160	167
49	420	459	272	140	156
73	348	338	314	150	148
105	250	262	372	135	138
146	225	213	402	136	136
208	170	177	481	135	128

It will be seen from these results and the corresponding curves in Figs. 3 and 4 that the length of the induction period is (*a*) directly proportional to the pressure of ammonia, (*b*) independent of the hydrogen pressure, and (*c*) increased at first slowly and later more rapidly as the pressure of the chlorine is decreased.

These results are not consistent with the view of Chapman and McMahon that the ammonia or its derivatives are removed from the system by the hydrogen chloride as it is formed, since the rate of production of the latter is dependent on the hydrogen pressure, while, according to (*c*) above, the induction period is independent of the hydrogen pressure. On the other hand, they do accord with the hypothesis that the ammonia is removed by reaction with the chlorine, which could occur according to the following equations :

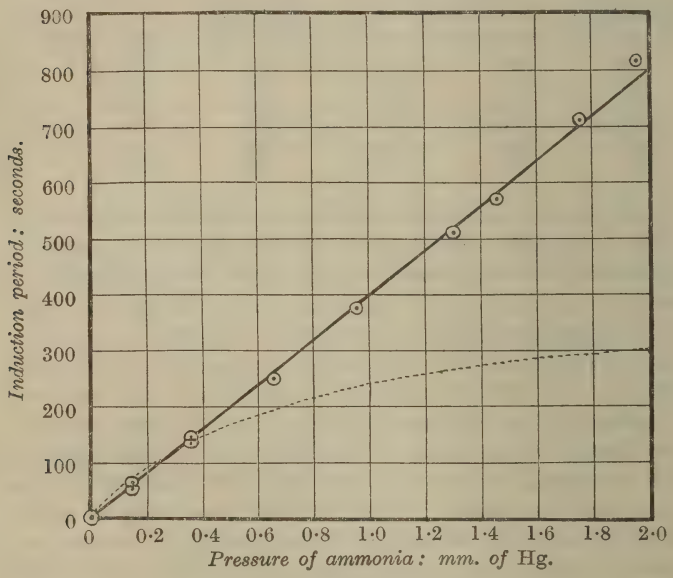
$$2NH_3 + 3Cl_2 = N_2 + 6HCl.$$
$$6HCl + 6NH_3 = 6NH_4Cl.$$

The production of ammonium chloride in the bulb was indeed confirmed by the analysis of an easily sublimable, white deposit which formed on the walls of the reaction chamber when it was used several times successively with high ammonia pressures. This deposit could easily be removed by warming the bulb and washing it out several times with air. A very dilute solution of the deposit in water gave a precipitate with Nessler's solution and a turbidity with silver nitrate, proving it to be ammonium chloride.

The results set forth in Figs. 3 and 4 cannot, however, be interpreted as due to a *homogeneous gaseous* reaction between the chlorine and ammonia, but are in agreement with the view that this reaction occurs on the illuminated surface of the vessel. Thus, in the presence of a large constant excess of chlorine, a homogeneous gaseous reaction would be unimolecular with respect to the ammonia, and the induction period, corresponding with the time required to remove the ammonia, would vary according to the dotted curve shown in Fig. 3; moreover, for constant pressures of ammonia, the induction period should vary in inverse ratio to the chlorine pressure, which is not found to be the case.

FIG. 3.

Variation of induction period with ammonia-pressure.



On the other hand, if it is assumed that the surface is at all times saturated with respect to ammonia, and that this is removed by reaction with the bombarding chlorine molecules under the influence of the light, a simple explanation is afforded of the above data. Let the whole surface water film, of area s, be covered with ammonia, and let a fraction, θ, at any moment be reacting with chlorine. The rate of evaporation of the products of this reaction will be proportional to this area, and may be written $\nu\theta s$, where ν is constant. The rate of reaction of chlorine will be proportional to the pressure of the chlorine (P) (*i.e.*, number of collisions with the surface per second) and to the disengaged ammonia surface, $(1 - \theta)\, s$. When

a steady state has set in at the surface, the rate of reaction between the ammonia and chlorine will equal the rate of evaporation of the products, and we may write therefore

$$v\theta s = kP(1 - \theta)s,$$

k being constant.

Whence $$\theta = kP/(\nu + kP).$$

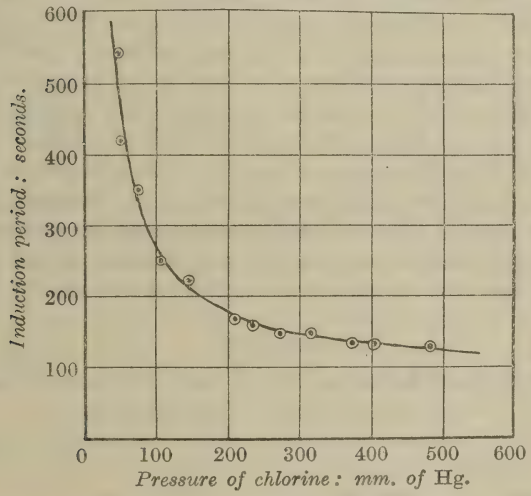
Hence the rate of destruction of the ammonia is

$$r = v\theta s = \nu kPs/(\nu + kP).$$

Let p be the pressure of ammonia introduced into the reaction vessel of volume v. Then the total quantity of ammonia to be removed

FIG. 4.

Variation of induction period with pressure of chlorine.



by this surface mechanism is measured by pv, and the time required is the induction period, T.

Hence $$T = pv/r = pv(\nu + kP)/s\nu kP.$$

Writing $1/\nu = a$ and $\nu/k = b$, we obtain $T = apv(1 + b/P)/s$.

If P, the pressure of the chlorine, and the illuminated surface, s, be maintained constant, we have the linear relationship between the initial pressure of ammonia and the induction period obtained experimentally and shown in Fig. 3.

If, on the other hand, the pressure of ammonia, p, and the illuminated surface be maintained constant, then the induction period depends on the chlorine pressure according to the relationship

$$T = k(1 + b/P).$$

Expressing T in seconds, and P in mm. of mercury, and giving to k and b the values 90 and 200 respectively, the curve of this equation has been plotted in Fig. 4; it will be seen that the deviation of the experimental points is in all cases small. The values for the induction period calculated according to this expression are also tabulated in the third column of Table III.

Finally, the formula for the induction period involves no term dependent on the hydrogen pressure, in conformity with the data of Table II.

As a final and crucial test of the expression developed above, it remained to show that the induction period is dependent on the volume of the reaction vessel and the extent of illuminated surface, by a suitable variation of the dimensions of the vessel A.

It will be seen that for constant pressures of chlorine $T/p \propto v/s$. A second bulb was therefore prepared of volume 45 c.c. and diameter 4·4 cm., and interchanged with the original one. The dimensions of the stops limiting the light were kept at the original magnitude (4 cm. in diameter), so that the change in the dimensions of the illuminated surface was relatively small. This was deemed necessary, since the field of illumination could not be considered uniform. Comparative runs with the two bulbs, as will be seen from the results of Table IV, showed unmistakably that the quotient Induction period/Pressure of ammonia is proportional to the volume of the vessel, when the illuminated surface s is kept constant.

TABLE IV.

Variation of Induction Period with Volume of Vessel.

Pressure of chlorine *ca.* 480 mm. of Hg.
Pressure of hydrogen 150—170 mm. of Hg.

Volume of vessel plus gauge (5 c.c.) = v c.c.	Pressure of ammonia, p, in mm. of Hg.	Induction period, T, in secs.	T/p.
50	1·77	180	1·02
	1·96	180	0·92
	1·78	185	1·04
		Mean value	1·00
190	See Table I.	Mean value	4·02

Thus the ratio of the volumes of the two bulbs is $190/50 = 3{\cdot}8$, whilst the ratio of the quotients T/p is $4{\cdot}02/1{\cdot}00 = 4{\cdot}02$, a sufficiently close agreement.

As a means of keeping the volume constant and varying the surface, a bulb containing glass wool was prepared, of 200 c.c. free space. The illuminated surface, limited by the same stops as previously, was in this way augmented by the irregular surface of the glass wool immediately in contact with the front face of the

bulb, and though the back face of the bulb now received no light, the total illuminated surface was considerably in excess of the surface of the bulb containing no glass wool. In spite of the fact that all the ammonia had now to diffuse to the forward surface of the bulb, through the interstices of the obstructing mass of glass wool, the induction period was markedly shortened, the quotient T/p being reduced from 4 to 3, as is shown by the results set out in Table V.

TABLE V.

Variation of Induction Period with Surface of Vessel.

Pressure of chlorine *ca.* 480 mm. of Hg.
Pressure of hydrogen *ca.* 160 mm. of Hg.

Reaction vessel.	Ammonia pressure, p, in mm. of Hg.	Induction period. T (secs.).	$T/p \times 10^{-2}$.
Original (volume 190 c.c.)	See Table I.		Mean value 4·02
Surface increased by glass wool (volume 205 c.c.).	2·0	600	3·00
	2·1	590	2·82
	2·1	620	2·95

These results (Tables IV and V) therefore show (other things being equal) that the induction period is (quantitatively) proportional to the volume of the reaction vessel and (qualitatively) inversely proportional to the illuminated surface, as required by the "surface poisoning hypothesis" developed in this paper. It would indeed be difficult to escape from the view, even if the evidence given in Part I were not available, that the sudden onset of the hydrogen–chlorine reaction, at the termination of the induction period, is due to the liberation of the illuminated surface from the adsorbed ammonia, and its consequent activation for the primary photochemical reaction of the hydrogen–chlorine system.

Summary.

The view developed in Part I is extended to account for the phenomenon of photochemical induction as a surface poisoning effect by ammonia derived from traces of nitrogenous impurities. Ammonia is assumed preferentially to combine with the catalytically active water film, and to require removal by photochemical reaction with the chlorine before the primary reaction can occur.

A quantitative study of the induction period, produced by adding known doses of ammonia to the hydrogen–chlorine system, has been undertaken. The results can be expressed by the formula

$$T = apv(1 - b/P)/s,$$

where T is the induction period, p, P are the pressures of ammonia

and chlorine, v and s are the volume and surface of the reaction vessel, and a and b are constants; and are consistent with the surface poisoning theory set out above.

The author desires to thank the Department of Scientific and Industrial Research for a maintenance grant which has made this work possible.

Department of Physical Chemistry,
Cambridge University. [*Received, June 17th,* 1925.]

CCCXVII.—*Selective Solvent Action. Part IV. Cryoscopy in Mixed Solvents.*

By Robert Wright.

The depression of the freezing point of a solvent produced by the addition of a solute may be diminished by the subsequent addition of a third substance; the diminution may be due to various causes based on the decrease in the concentration of the solute molecules or complexes in the solution.

In recent papers (J., 1922, **121**, 2252; 1923, **123**, 2493; 1924, **125**, 2068) dealing with the partial vapour pressures of aqueous alcohol, it has been shown that a substance soluble in only one constituent of the aqueous alcohol will, when added to the mixed solvent, lower the vapour pressure of the constituent in which it is soluble and raise the vapour pressure of the other. The formation of solvates would account for this behaviour. Similar results might be expected from a study of the freezing points of such systems. Mihaly (*Z. physikal. Chem.*, 1897, **24**, 13) observed that the addition of water to the mixed solvents alcohol–benzene, phenol–benzene, and acetic acid–benzene raised the freezing point of the benzene, and attributed the results to the formation of hydrates. A cryoscopic examination was therefore made of a considerable number of semi-solutes in the mixed solvents named in Table I (alcohol–water gave indefinite freezing points). As a rule, no difficulty was found in determining the freezing points to 0·02° by the ordinary Beckmann method.

As anticipated, the freezing point of the constituent in which the semi-solute is insoluble is always raised by the addition of the semi-solute. When the concentration of the latter is plotted against the elevation of the freezing point a continuous curve results with a break at the point of formation of two liquid phases.

The insolubility of the solutes in the first constituent of the mixed solvent was tested by noting the effect of excess of the solute on

Table I.

Nicotine–Water.

40 C.c. of nicotine in 100 c.c. of water. Density 1·007. F. p. of solution −2°. 20 C.c. of solution used as solvent.

w = wt. in g. of the third substance and $e°$ = elevation of the f. p.

Benzene :	w	0·0770	0·1385	0·2130*	0·2977	0·3185	
	$e°$	0·030	0·048	0·072	0·081	0·083	
Carbon tetrachloride :							
	w	0·0965	0·2020	0·2985*	0·3995	0·5250	
	$e°$	0·010	0·022	0·027	0·030	0·031	
Chloroform :	w	0·0795	0·1640	0·3020	0·4070*	0·5220	0·6535
	$e°$	0·023	0·036	0·075	0·095	0·115	0·126
Methyl salicylate :	w	0·0655	0·1430	0·2145	0·2955*	0·3920	0·5070
	$e°$	0·043	0·063	0·108	0·125	0·125	0·125
Monobromonaphthalene :							
	w	0·0460	0·0975*	0·1375	0·1780	0·2170	
	$e°$	0·045	0·060	0·068	0·070	0·070	

Alcohol–Benzene.

25 C.c. of alcohol in 100 c.c. of benzene. Density 0·853. F. p. of benzene 5·5°. F. p. of solution 1·3°. 20 C.c. of solution used as solvent.

Citric acid :	w	0·0220	0·0330	0·0445	0·0625	0·1035	excess
	$e°$	0·060	0·100	0·145	0·180	0·250	0·770
Tartaric acid :	w	0·0130	0·0350	0·0495	0·0667	0·0870	excess
	$e°$	0·030	0·090	0·118	0·155	0·197	0·367
Oxalic acid :	w	0·0280	0·0590	0·0880	0·1235	0·1550	excess
	$e°$	0·065	0·135	0·200	0·295	0·355	2·100
Cadmium iodide :	w	0·0482	0·1132	0·2027	0·3092	0·4127	excess
	$e°$	0·042	0·083	0·125	0·190	0·252	1·105

Acetone–Benzene.

20 C.c. of acetone in 100 c.c. of benzene. Density 0·856. F. p. of solution −6·2°. 20 C.c. of solution used as solvent.

Mercuric chloride :	w	0·1375	0·2035	0·3245	0·4370	excess
	$e°$	0·130	0·200	0·290	0·420	0·920
Cadmium iodide :	w	0·0730	excess			
	$e°$	0·110	0·480			

Alcohol–Ethylene Dibromide.

25 C.c. of alcohol in 100 c.c. of ethylene dibromide. Density 1·888. F. p. of ethylene dibromide 9·5°. F. p. of solution 5°. 20 C.c. of solution used as solvent.

Oxalic acid :	w	0·0938	0·1561	0·2298	0·3073	0·4083	0·5028*	0·6001
	$e°$	0·175	0·298	0·448	0·610	0·795	0·970	1·115
	w	0·7555	0·9523	1·1182	excess			
	$e°$	1·375	1·615	1·755	2·080			
Citric acid :	w	0·1140	0·2032	0·2875	0·4058	0·6365*	excess	
	$e°$	0·170	0·275	0·410	0·590	0·830	1·030	
Tartaric acid :	w	0·1060	0·1805	0·3360	excess			
	$e°$	0·160	0·260	0·440	0·480			
Water :	w	0·0710	0·1365*	0·2335	0·3025	0·4005	0·4830	0·6510
	$e°$	0·250	0·510	0·780	0·950	1·110	1·210	1·470

* System separates into two liquid phases.

the freezing point of the pure constituent. Thus excess of water lowered the freezing point of ethylene dibromide by 0·08° and mercuric chloride lowered the freezing point of benzene by 0·05°. The effect produced by all other solutes was less than 0·02°.

It thus seems evident that a semi-solute when dissolved in a mixed solvent forms solvates with the constituent in which it is soluble, and as a result raises both the freezing point and the vapour pressure of the other constituent. Thus the addition of alcohol to benzene lowers the freezing point of the latter and—on the solvate theory—forms alcohol–benzene complexes. The subsequent addition of water decomposes some of these with the formation of water–alcohol complexes; benzene is thus liberated and a more dilute solution with a higher freezing point is produced.

An attempt was made to carry the investigation a step further by adding glucose to the homogeneous solvent consisting of 10 c.c. of benzene, 10 c.c. of alcohol, and 2 c.c. of water, but the results obtained were too indefinite to be of any value.

The effect of solutes soluble in both constituents of a mixture of equal weights of alcohol and benzene was also examined. The solutes used were acetanilide (11), benzoic acid (4), picric acid (0·8), naphthalene (0·3), and phenanthrene (0·08). The figures after each substance indicate roughly the ratio of its solubility in alcohol to that in benzene.

Table II shows that the solutes which are more soluble in alcohol at first raise the freezing point of the benzene and afterwards, at higher concentrations of solute, depress it; whilst those substances which are more soluble in benzene than in alcohol depress the freezing point of the benzene at all concentrations. This may be explained by the view that the substances more soluble in alcohol form solvates with the alcohol more readily than with the benzene, and only at higher concentrations, where the alcohol is to some extent bound, does the depression of the freezing point of the benzene take place. On the other hand, substances more soluble in benzene naturally depress the freezing point in all concentrations.

If it may be concluded from the above results that a substance which at first raises the freezing point of the benzene in the 50% alcohol–benzene mixture and then depresses it is more soluble in alcohol than benzene, whilst a substance which, even in low concentration, depresses the freezing point of the benzene is more soluble in it than in the alcohol; then the method may be applied to discriminate between the relative attractions of benzene and alcohol for a third liquid which is completely miscible with both. Thus if acetic acid has a greater attraction for alcohol than benzene, it will at low concentrations raise the freezing point of the benzene in the

Table II.

Changes in the freezing point of benzene in a 50% (by weight) alcohol–benzene mixture produced by solutes soluble in both constituents of the solvent. F. p. of solution −5·5°. 20 C.c. of solution used as solvent.

w = wt. in g. of the third substance and e = elevation of the f. p.

Acetanilide.		Benzoic acid.		Naphthalene.	
w.	*e.*	*w.*	*e.*	*w.*	*e.*
0·0125	0·09°	0·0475	0·03°	0·0885	−0·18°
0·0268	0·18	0·1065	0·03	0·2130	−0·50
0·0420	0·20	0·2190	−0·06	0·3740	−1·11
0·0767	0·23	0·3545	−0·33		
0·1135	0·38	0·4870	−0·47		
0·1660	0·28			Phenanthrene.	
0·2300	0·18	Picric acid.		0·0335	−0·07
0·3145	0·13	0·0805	−0·04	0·0647	−0·10
0·4090	0·06	0·1775	−0·16	0·1170	−0·30
0·5620	−0·03	0·3255	−0·38	0·2145	−0·51
0·7030	−0·14	0·5045	−0·53	0·3100	−0·73
		0·6900	−0·83		

Changes in the freezing point of benzene in a 50% (by weight) alcohol–benzene mixture produced by solutes completely miscible with each constituent of the mixture. 20 C.c. of the solution used as solvent.

Methyl alcohol.		Propyl alcohol.		*iso*Butyl alcohol.		*tert.*-Amyl alcohol.	
w.	*e.*	*w.*	*e.*	*w.*	*e.*	*w.*	*e.*
0·0450	0·07°	0·0570	0·06°	0·0300	0·13°	0·0420	0·00°
0·0905	0·17	0·1250	0·05	0·0650	0·10	0·0740	0·00
0·1490	0·16	0·2235	0·01	0·1110	0·06	0·1070	0·00
0·2215	0·18	0·4020	−0·19	0·1740	0·04	0·1490	−0·02
0·3250	0·17	0·6160	−0·46	0·2715	0·03	0·2185	−0·09
0·4740	0·01			0·3960	−0·04	0·2950	−0·09
0·5780	−0·17					0·3930	−0·08
0·7780	−0·25					0·5530	−0·14
						0·6710	−0·24
						0·8720	−0·38

n-Heptyl alcohol.		Octyl alcohol.		Acetic acid.		Propionic acid.	
0·0315	0·00	0·0375	−0·02	0·0385	0·00	0·0400	−0·01
0·0655	0·00	0·0810	−0·04	0·0955	0·00	0·0860	−0·07
0·1130	−0·09	0·1405	−0·06	0·1770	−0·17	0·1770	−0·09
0·1780	−0·17	0·2120	−0·14				
0·2840	−0·30						

Butyric acid.		Toluene.		Ethylbenzene.		Nitrobenzene.	
0·0415	−0·02	0·0570	−0·20	0·0442	−0·23	0·0630	−0·12
0·0890	−0·02	0·1100	−0·38	0·1432	−0·66	0·1170	−0·19
0·1845	−0·08	0·1690	−0·76	0·2272	−1·03	0·2650	−0·35
0·3450	−0·36						

Aniline.		Benzyl alcohol.		Phenylethyl alcohol.		Carbon tetrachloride.	
0·0565	−0·03	0·0555	−0·06	0·0505	−0·06	0·0650	−0·06
0·1345	−0·11	0·1310	−0·11	0·1225	−0·14	0·1260	−0·13
0·2295	−0·23	0·2450	−0·23	0·2640	−0·28	0·2425	−0·28

50% mixture, but if the acid has a greater attraction for the benzene it will lower its freezing point at all concentrations.

The results are tabulated for sixteen miscible solutes and it will be seen that the lower members of the fatty alcohol series show a

greater attraction for ethyl alcohol than for benzene. Amyl alcohol up to a considerable concentration has little effect on the freezing point of benzene in the mixed solvent and may therefore be considered to have almost equal attractions for the two constituents. On the other hand, the higher alcohols and the aromatic compounds in general all seem to show a greater attraction for benzene than for alcohol.

A similar phenomenon is met with when a solute is distributed between two liquids with both of which the solute is miscible. Thus acetic acid is miscible both with water and with benzene, but measurements of the partition coefficient show that the acid is much more strongly attracted by the water than by the benzene. The same results are obtained when the acid is partitioned between water and carbon tetrachloride or water and toluene. Miscibility might therefore be considered rather as indefinite than infinite solubility.

The mixed solvent was prepared from equal weights of the two constituents. The usual method of freezing-point determinations was employed, but owing to the great concentration of the alcohol in the 50% mixture the results are not very accurate, though there was little difficulty in getting readings to within 0·05°. The results, however, are only of a qualitative nature and great accuracy is not claimed for them.

GLASGOW UNIVERSITY. [*Received, July 15th*, 1925.]

CCCXVIII.—*Colour and Molecular Geometry. Part IV. Explanation of the Colours of the Cyanine Dyes.*

By JAMES MOIR.

THE conception (this vol., p. 968) that the height of colour depends in the majority of cases mainly on the distance between two positive centres in the molecule may be applied to all classes of coloured substances. In many familiar commercial dyes, however, the molecule contains extensive inactive parts, lying outside the two positive centres. These inactive parts produce a "loading" effect on the colour, raising the position of the absorption band by an amount varying between $\frac{1}{2}$ and 10%. The cyanines, *iso*cyanines, *ψ-iso*cyanines, azocyanines, and carbocyanines belong to this class. Before any explanation of their colours can be attempted it is necessary to estimate in quantitative terms the effect of the "load." This would have been unnecessary if all the parent substances had been made and their spectra measured.

The parent substances of these compounds are, respectively, di-4-pyridylmethane, $(C_5NH_4)_2CH_2$, 2 : 4′-dipyridylmethane, di-2-pyridylmethane, di-2-pyridylamine, $(C_5NH_4)_2NH$, and (for the three kinds of carbocyanine) 4 : 4′-, 2 : 4′-, and 2 : 2′-dipyridylpropenes, $C_5NH_4{\cdot}CH_2{\cdot}CH{:}CH{\cdot}C_5NH_4$. Miss Hamer was kind enough to present me with a specimen of di-2-quinolylamine, and I have succeeded in making the third substance and its methyl derivatives. Observations of these were sufficient, taken along with published data, to solve the problem.

Scheibe and Rossner (*Ber.*, 1921, **54**, 786) made the very significant discovery that di-2-quinolylmethane, which is a nearly colourless substance, can be converted by dilute acid, at about $p_H = 5$, into a coloured phase which has practically the same absorption spectrum as *ψ-iso*cyanine (which is the dimethyl derivative of this diquinolylmethane). The colour of the *ψ-iso*cyanine salts is therefore due to the stable activation of the molecule by the methyl groups, which render the nitrogen atom (or possibly both nitrogen atoms) permanently quinquevalent.

There is a minute difference between the colours of *ψ-iso*cyanine salts and of activated di-2-quinolylmethane : the observations show that the methyl " colour-factor " has the value 1·005 (λ 521 for the former, and λ 516 * for the latter—referring to the highest band of each : the square root of the ratio of these figures is the methyl colour-factor).

Similarly, comparison of my observations on activated diquinolylmethane with those on activated dipyridylmethane enables the colour-factor for quinolyl/pyridyl to be calculated; the top band of the latter is at λ 422, whence the colour-factor is $\sqrt{516/422}$, or 1·105.

This figure is much the same as the naphthol/phenol colour-factor previously established in the ordinary dicyclic family of dyes. It shows that the effect of the extra " loading " with a portion of a benzene ring is the same in the two families of colouring matters.

Two other interesting regularities emerge from the observations. (A) All the cyanines have two bands close together, and the ratio of the absorption-centre wave-lengths for the two bands of each substance is practically always 1·065. (B) By a remarkable coincidence also the change of linking from ortho to para [*i.e.*, the change from 2 : 2′ (or *ψ-iso*) to 2 : 4′ (or *iso*), and from *iso* to ordinary (2 : 4′ to 4 : 4′)] involves the same factor 1·065.

These factors therefore cancel in certain cases : the lower band of a 4 : 4′-cyanine is in the same place as the higher band of the

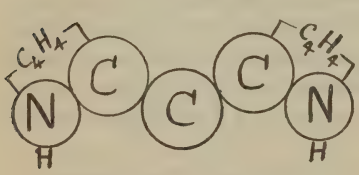
* Author's observations in water : 4 units higher in alcohol.

corresponding 2 : 4′-cyanine, and the lower band of the latter is in the same place as the higher band of the corresponding 2 : 2′-cyanine.

The whole of the family having thus been regularised, it is only necessary to consider a single example, *viz.*, the simplest one, di-2-pyridylmethane, in order to find the distance between the positive centres on which the colour depends.

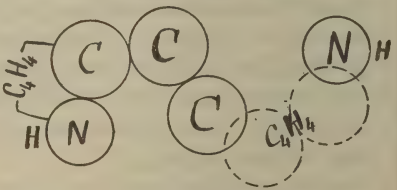
The formula of this substance may be written $C_4H_4NC{\cdot}C{\cdot}CNC_4H_4$ (H_2), in which the atoms in positions 3, 4, 5, and 6 of the pyridine rings are written as C_4H_4. For the molecule in the activated condition, this becomes $C_4H_4(NH)C{:}C{:}C(NH)C_4H_4$. Since the C_4H_4 groups lie obliquely to the chain NCCCN a small allowance may be made for this type of "loading" (see J., 1924, **125**, 1139). The activated substance being found to have λ 422, the value λ 415 may be attributed to the chain NCCCN. From the graph in Part III the distance between the centres of the nitrogen atoms in this chain is found to be 5·33 tenth-metres.

FIG. 1.



Di-2-pyridylmethane.

FIG. 2.



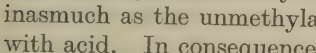
2 : 4′*Dipyridylmethane.*

Now if the five atoms were in a straight line, the distance would be (using Bragg's data) (3 × 1·54) + (2 × 0·65) or 5·92 tenth-metres. If the five atoms are arranged alternately (zigzag) at 109½°, *viz.*, N–C–C–C–N, the distance between the nitrogen centres is about 4·9 tenth-metres. If they are arranged in the same manner but with the double-bond angle of 125¼° between each carbon atom, *viz.*, N–C=C–C–N, the distance is at 5·26 tenth-metres; which is sufficiently near what is required. Fig. 1 represents the result drawn to scale. It is to be noted that the central carbon atom is almost in line with the two nitrogen atoms. The diagram for dimethyl-ψ-*iso*cyanine iodide would be the same, with C_8H_6 for C_4H_4, two methyl groups on the nitrogen atoms, and HI added. The diagram for dimethyl*iso*cyanine iodide would be as the foregoing, but with one nitrogen para to the central carbon atom, as shown for its parent-substance, 2 : 4′-dipyridylmethane, in Fig. 2. Since the shape of the pyridine ring is not yet known, Fig. 2 cannot

be drawn to scale. Similarly, if both nitrogen atoms are para to the central carbon atom, the distance between the nitrogen centres is still farther increased, and the diagram for ordinary cyanine (which is blue, with λ 590, when examined in water) is obtained.

In the opinion of the author the subsidiary band of the cyanines is to be accounted for by a small alteration in one of the angles of the (otherwise rigid) configuration shown, say from 125° to 109°.

The azocyanine family appears to be abnormal in one respect, inasmuch as the unmethylated member does not become activated with acid. In consequence the effect of the methyl groups is large (factor 1·06 instead of 1·005; see p. 2339).

The carbocyanines probably have the zigzag arrangement  , in which all the angles are $125\frac{1}{4}°$, except one, which is smaller. On account of the great "loading" the distance between the nitrogen centres need not be greater than 6 or $6\frac{1}{2}$ tenth-metres to agree with the high colour of these substances. The other factors have the same effect in this series as in the cyanine series (kryptocyanine λ 711, 2 : 4′-carbocyanine λ 657, pinacyanole λ 607).

The author's restrictive definition of the term "auxochrome" must be expanded to meet these cases, for it is obvious that nitrogen in a ring is the auxochrome of the cyanine family quite independently of its being alkylated or not: similarly, oxygen in a ring is the auxochrome of the natural phenylbenzopyranole colours and also of fluorescein in its acid phase. The terms auxochrome and hapton really connoted an intermediate stage in the rejection of the German theory of colour, and are now themselves generalised and replaced by the conception of two positive centres; a conception which, combined with that of comparative molecular rigidity, is probably capable of explaining all colour phenomena (Part III, *loc. cit.*).

Experimental.

The syntheses were all performed by adding phosphorus pentachloride to a warm mixture of quinaldine (or methylquinaldinium iodide, or picoline, or methylpicolinium iodide, according to the substance required) and 2-pyridone (or carbostyril). The latter two substances were made from pyridine or quinoline by means of hypochlorous acid (Einhorn and Lauch, *Annalen*, 1888, **243**, 343). The yield is poor; but the materials are cheap.

Di-2-pyridylmethane, from picoline and 2-pyridone, is deep yellow in water containing a little alcohol and acetic acid: λλ about 422 and 399. In the unactivated condition it is pale, and the upper band is absent.

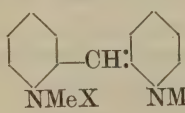
1-Methyldi-2-pyridylmethane, from methylpicolinium iodide and 2-pyridone, appears to be yellow (activated) under all conditions: λλ about 425 and 400.

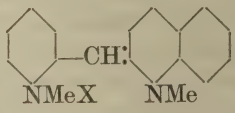
2-Pyridyl-2-quinolylmethane, from quinaldine and pyridone or from picoline and carbostyril, is orange when activated and yellow when neutral. The bands are vague, but are roughly at λλ 460 and 434. There are two possible *N*-methyl derivatives of this substance, *viz.*, quinolyl-methylpyridyl-methane, $C_9H_6N{\cdot}CH{:}C_5H_4NMe$ or $C_9H_7N{:}C{:}C_5H_4NMe$, and pyridyl-methylquinolyl-methane, $C_5H_4N{\cdot}CH{:}C_9H_6NMe$ or $C_5H_5N{:}C{:}C_9H_6NMe$. Both are orange-brown in dilute acetic acid, but the preparations were unsatisfactory; both have much the same absorption, in which the upper band is abnormally faint: observed λλ 488 and 460.

Di-2-quinolylmethane, from quinaldine and carbostyril, is, as Scheibe states, pale in colour, but can be activated by dilute acetic acid so as to exhibit the high colour of dimethyl-*ψ-iso*cyanine salts. The lower band is at about λ 490 (see p. 2339 for the comparison with the cyanine).

The 1-methyl derivative of the foregoing has a colour and a spectrum almost identical with those of dimethyl-*ψ-iso*cyanine iodide: observed λλ 519 and 490.

Small quantities of the unknown primitive cyanines have been prepared. 1 : 1′-Dimethyldi-2-pyridylmethane hydroxide anhydride (I) (which the author suggests should be named dimethylprotocyanine) is yellow in solution with λλ 428 and 405. It is the

(I.) 



(II.)

pyridine analogue of dimethyl-*ψ-iso*cyanine. The intermediate substance (II) is orange in solution and has apparently three bands, at λλ 495, 465, and 430, the lowest being the strongest. The author suggests the name dimethylmesocyanine for this substance.

Observations in water of Miss Hamer's nitrogen-analogues of the 2 : 2′-cyanines (J., 1924, **125**, 1348) gave the following results:

Dimethylazocyanine: λλ 421 and 396 (this is 4 units lower than the discoverer's observation in alcohol).

Methyldiquinolylamine (termed by Miss Hamer methyldihydroquinolenylquinolylimine): λλ 420 and 394.

Di-2-quinolylamine in acetic acid: λλ 371 and 350.

2-Aminoquinoline in acetic acid: λ 340 broad (similar to carbostyril: λ 327).

Both diquinolylamine and dimethylazocyanine have the same

absorption in concentrated sulphuric acid solution, *viz.*, narrow bands at λλ 375 and 358.

Summary.

1. The positions of the bands of the cyanines are calculated by multiplying those of the *iso*cyanines by 1·065.

2. Those of the *iso*cyanines are obtained from those of the *ψ-iso*-cyanines by means of the same factor.

3. Those of the *ψ-iso*cyanines are practically the same as those of di-2-quinolylmethane activated by very weak acid.

4. Those of diquinolylmethane are derived from those of dipyridylmethane by multiplying by the square of the factor 1·105.

5. The bands of activated dipyridylmethane are explained on the author's spatial theory of colour.

6. The factor 1·065 (for calculating the positions of the bands of 4 : 4′-compounds from those of 2 : 4′-compounds or 2 : 4′-compounds from those of 2 : 2′-compounds) holds good also in the carbocyanine series.

GOVERNMENT LABORATORY, JOHANNESBURG. [*Received, May 11th*, 1925.]

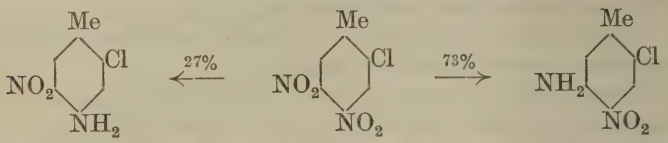
CCCXIX.—*The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. Part VIII.* 2 : 3- *and* 2 : 5-*Dinitro*-p-*chlorotoluenes.*

By JAMES KENNER, CHARLES WILLIAM TOD, and ERNEST WITHAM.

IT is well recognised that, in spite of much careful work, pre-eminently by Holleman, our present knowledge of the processes of substitution of the benzene nucleus does not permit complete confidence in forecasting the behaviour of more complicated derivatives towards substituting agents. The discussions in previous papers of this series indicate that this difficulty is perhaps less marked in the case of the mobility of substituents in aromatic nitro-derivatives; some instances of exceptional behaviour, however, are on record (compare, *e. g.*, Robinson and Robinson, J., 1917, **111**, 944).

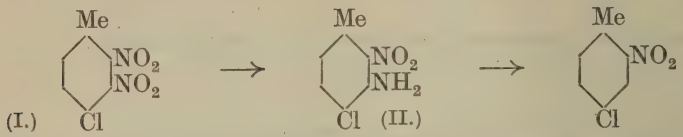
The difference between the two cases possibly lies in the fact that in ordinary substitution we do not yet know how to determine from which point, if any, in the nucleus to calculate the directive effect, whereas it seems clear that the mobility referred to is primarily determined by nitro-groups and that ortho-para-directive substituents produce subsidiary effects only. In certain cases, however, these are decisive, and it is therefore of importance to compare

the effects produced by different substituents. For example, Morgan and his collaborators (J., 1920, **117**, 784; 1921, **119**, 1537) showed that 2-chloro-4 : 5-dinitrotoluene, on treatment with alcoholic ammonia, is converted into a mixture of the two possible chloronitrotoluidines, in which the *m*-derivative predominates :



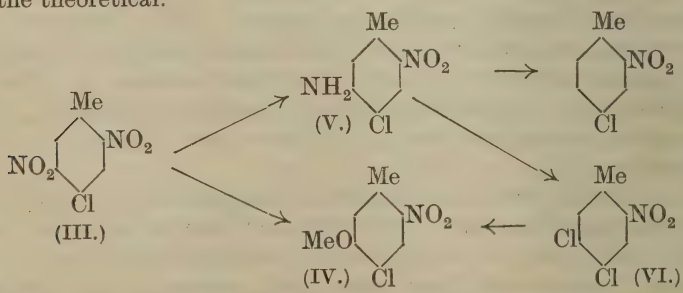
We have now supplemented this result by experiments on 4-chloro-2 : 3-dinitrotoluene (I) and the corresponding 2 : 5-derivative (III).

4-*Chloro*-2 : 3-*dinitrotoluene*, prepared from 2 : 3-dinitro-*p*-toluidine (Scott and Robinson, J., 1922, **121**, 844), was converted by methyl-alcoholic ammonia at 150° into 4-*chloro*-2-*nitro*-m-*toluidine* (II), which was isolated to the extent of 70% of that theoretically possible :



As indicated, the constitution of the product was established by its conversion into the known 4-chloro-2-nitrotoluene. No 4-chloro-3-nitro-*o*-toluidine was isolated in these experiments.

4-*Chloro*-2 : 5-*dinitrotoluene* was similarly converted into a mixture of products, from which, by a somewhat lengthy process of separation, 4-*chloro*-6-*nitro*-m-*tolyl methyl ether* (IV), accompanied by a small quantity of the *m*-cresol itself, and 4-*chloro*-6-*nitro*-m-*toluidine* (V) were obtained, the yields being respectively 20 and 30% of the theoretical.



By elimination of the amino-group, the base (V) furnished 4-chloro-2-nitrotoluene, whilst in order to establish the constitution of the methyl ether (IV), the base was converted into a 4 : 5-*dichloro*-

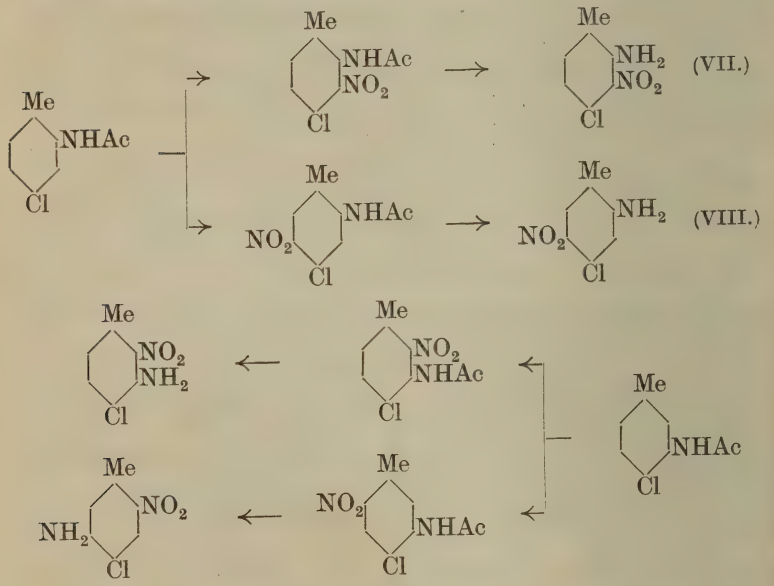
2-*nitrotoluene* (VI), from which a product identical with the ether was easily prepared by treatment with sodium methoxide. No other definite products could be isolated from the above mixture, and it appeared that the tarry residues consisted of azo- or azoxy-derivatives.

In each of the three chlorodinitrotoluenes, therefore, the group that is displaced is the one in the meta-position to the methyl group rather than that in the meta-position to the chlorine atom, and it cannot be doubted that some fundamental difference between these substituents is here involved. If we accept the evidence, derived from the behaviour of 3 : 4-dinitrotoluene (Kenner and Parkin, J., 1920, **117**, 852) and 3 : 4-dinitrochlorobenzene (Laubenheimer, *Ber.*, 1876, **9**, 1826; 1878, **11**, 1156), respectively, that each of them favours the mobility of nitro-groups in the meta-position, the influence of the methyl group is seen to be stronger than that of the chlorine atom, a result in direct contrast with that arrived at by Holleman from the study of direct substitution.

It would be premature to deduce any general conclusion from this single instance, but it is not at once obvious how such a contradiction is reconcilable with the theory of alternate strong and weak bonds. According to the principle of induced alternate polarities, on the other hand, direct substitution consists in the replacement of a positive hydrogen atom, whilst mobile substituents are negative, so that a difference of the kind now revealed is conceivable. As against this, it has recently been suggested that the behaviour of nitrosobenzene on substitution "distinctly favours" the alternate strong and weak bond theory (Ingold, this vol., p. 515). In reality, however, there is here a confusion of issues. For, although it is claimed that the principle of alternate polarities operates in the benzene nucleus and determines the point of substitution, it has also been pointed out (Robinson, *Ann. Reports*, 1922, **19**, 102; compare also Allsop and Kenner, J., 1923, **123**, 2296) that erroneous conclusions may arise from writing positive and negative signs in any group whatsoever. In such circumstances, the only proper procedure in investigating the validity of the polarity principle consists in determining, from its directive effect, which sign must, according to the principle, be assigned to a given group, and then ascertaining whether this conclusion accords with the general behaviour of the group in other directions. Thus Ingold's result would indicate that the nitroso-group is negative and hence should be comparable with chlorine and hydroxyl, so that the typical behaviour of these, when "positive" properties are imposed on them, as in hypochlorous acid and hydrogen peroxide, should be reproduced by nitrous acid. This is well known to be the case in

the reaction with hydrogen iodide, so that Ingold's result cannot be accepted as evidence against the polarity principle. It remains, of course, to be explained why the nitroso-group as a whole reacts as though endowed with negative properties, and it seems questionable whether valid evidence on this point can be deduced from reactions, *e.g.*, those with the Grignard reagent and with ethyl malonate, in which the group is broken up.

In order to place the above results on a still surer foundation, the bases already mentioned, together with those alternatively possible, namely 4-*chloro*-3-*nitro*-o-*toluidine* (VII) and 4-*chloro*-5-*nitro*-o-*toluidine* (VIII), were synthesised by the aid of reactions briefly represented in the following scheme :



Experimental.

Nitration of 4-*Chloroaceto*-o-*toluidide*.—A mixture of the finely-powdered compound (20 g.) with glacial acetic acid (30 c.c.) and sulphuric acid (40 c.c.) was thoroughly stirred and maintained at 10—15° during the addition of fuming nitric acid (*d* 1·5; 6 c.c.). After diluting the resulting stiff paste with ice-water, the solid material was collected, dried, and hydrolysed by boiling with 50% sulphuric acid (400 c.c.). From the mixture of weak bases precipitated by dilution with water, 4-*chloro*-5-*nitro*-o-*toluidine*, m. p. 163—164° (Found: N, 15·4. $C_7H_7O_2N_2Cl$ requires N, 15·0%), was isolated by crystallisation from benzene. Its *acetyl* derivative,

prepared by using a mixture of acetic anhydride and acetyl chloride, separated from benzene in prisms, m. p. 181—182° (Found : N, 12·3. $C_9H_9O_3N_2Cl$ requires N, 12·3%). 5-*Chloro*-2-*methyl*-p-*phenylenediamine*, obtained from the nitro-base by reduction in glacial acetic acid solution with stannous chloride and hydrochloric acid, crystallised from benzene–light petroleum in white leaflets, m. p. 145—146° (Found : N, 17·9. $C_7H_9N_2Cl$ requires N, 18·1%). The compound, m. p. 146°, of unknown orientation prepared by Vorländer (*Ber.*, 1901, **34**, 1652) from *N*-nitroso-*o*-tolylglycine was doubtless the same. The base responded to Lauth's test, and its acetyl derivative melted at 301°. The hydrochloride was prepared by Vehrmann (*Ber.*, 1915, **48**, 2028) from 4-chloro-2 : 5-dinitrotoluene.

4-*Chloro*-3-*nitro*-o-*toluidine*, light brown needles, m. p. 60—62·5°, was contained in the mother-liquors from the crystallisation of the 5-nitro-isomeride, and isolated by distillation in steam and repeated crystallisation from benzene–light petroleum (Found : N, 15·2. $C_7H_7O_2N_2Cl$ requires N, 15·0%). The *acetyl* derivative, m. p. 194—195°, prepared by means of acetic anhydride in presence of sulphuric acid, separated from benzene in small prisms (Found : N, 12·5. $C_9H_9O_3N_2Cl$ requires N, 12·3%).

Nitration of 4-*Chloroaceto*-m-*toluidide*.—This compound, previously described by Goldschmidt and Hönig (*Ber.*, 1886, **19**, 2411) as melting at 97°, was obtained in white needles, m. p. 102°. The nitration of the material, and hydrolysis of the product were performed as described in the case of the *o*-isomeride. Finally, steam was passed directly into the acid hydrolysis mixture until the melting point of the solid distillate was above 50°.

4-*Chloro*-6-*nitro*-m-*toluidine* was obtained after diluting the liquor in the distillation flask with hot water and filtering from tarry matter; it crystallised from dilute alcohol in yellow needles (15 g.), m. p. 120—121° (Found : N, 15·2. $C_7H_7O_2N_2Cl$ requires N, 15·0%). It was converted by reduction into 5-chloro-2-methyl-*p*-phenylenediamine, and its *acetyl* derivative, prepared by means of acetic anhydride and sulphuric acid, separated from dilute alcohol in white leaflets, m. p. 134—135° (Found : N, 12·3. $C_9H_9O_3N_2Cl$ requires N, 12·3%).

4-*Chloro*-2-*nitro*-m-*toluidine* was the chief constituent of the above solid steam-distillate. It was redistilled from 50% sulphuric acid solution with steam and then crystallised from dilute alcohol, lemon-yellow needles (4 g.), m. p. 52—53°, being thus obtained (Found : N, 15·1. $C_7H_7O_2N_2Cl$ requires N, 15·0%). The orientation of the base follows from its identity with the base obtained from 4-chloro-2 : 3-dinitrotoluene (*v. infra*). Its *acetyl* derivative, m. p. 210—212°, prepared by means of acetic anhydride, separated from

absolute alcohol in small prisms (Found : N, 12·7. $C_9H_9O_3N_2Cl$ requires N, 12·3%).

4-*Chloro*-6-*nitro*-m-*tolyl Methyl Ether*.—4-Chloro-6-nitro-*m*-toluidine (5 g.) was diazotised by Gattermann's method (*Annalen*, 1912, **393**, 200) by solution in nitrosylsulphuric acid (33 g. equiv. to 1·8 g. of sodium nitrite). The solid produced on adding the cooled solution to a solution of cuprous chloride (2 g.) in hydrochloric acid (18 g.) at 0° was collected and distilled in steam. 4 : 5-Dichloro-2-nitrotoluene (3 g.), thus obtained, separated from methyl alcohol in yellow needles, m. p. 63° (compare Cohen and Dakin, J., 1902, **81**, 1349). When the dichloro-compound (3 g.) was heated at 100° with a solution of sodium (0·3 g.) in methyl alcohol (12 c.c.) for 7 hours, the solution became neutral and contained 4-*chloro*-6-*nitro*-m-*tolyl methyl ether* (2·33 g.), which separated from methyl alcohol in light straw-coloured needles, m. p. 121—122° (Found : N, 7·1. $C_8H_8O_3NCl$ requires N, 6·9%).

4-*Chloro*-2 : 3-*dinitrotoluene*.—This compound, prepared from 2 : 3-dinitro-*p*-toluidine (Scott and Robinson, *loc. cit.*; Page and Heasman, J., 1923, **123**, 3235) by the process described in the case of 4 : 5-dichloro-2-nitrotoluene, crystallised from benzene–light petroleum in long, lemon-yellow prisms, m. p. 106·5° (Found : N, 13·1. $C_7H_5O_4N_2Cl$ requires N, 12·9%).

Action of Methyl-alcoholic Ammonia on 4-*Chloro*-2 : 3-*dinitrotoluene*.—The chloro-compound (4·32 g.) was heated with methyl alcohol (54 c.c.) and ammonia (*d* 0·880; 10 c.c.) for 8 hours at 140—150°. After removing alcohol from the product and distilling the residue in steam, a solid material (3·8 g.) was obtained in a practically pure condition. It separated from dilute alcohol in light yellow needles, m. p. 52—53°, and was identified as 4-chloro-2-nitro-*m*-toluidine (*a*) by comparison with an authentic specimen and (*b*) by degradation to 4-chloro-2-nitrotoluene by adding a diazotised solution of the base (1 g.) in nitrosylsulphuric acid (6·6 g.) to boiling absolute alcohol (200 c.c.) and distilling the product in steam after removal of the alcohol.

Action of Methyl-alcoholic Ammonia on 4-*Chloro*-2 : 5-*dinitrotoluene*.—The chloro-compound, prepared by Kehrmann's method (*Annalen*, 1898, **303**, 1; *Ber.*, 1915, **48**, 2028), was heated with the same proportions of methyl alcohol and ammonia as the 2 : 3-isomeride, but for 16 hours at 160°. The product left after removing the alcohol was extracted with six successive quantities of boiling concentrated hydrochloric acid (50 c.c.). The residue (0·86 g., m. p. 100—104°), after treatment with benzene to remove tarry material, furnished almost pure 4-chloro-6-nitro-*m*-tolyl methyl ether (0·63 g.), which did not depress the melting point of an authentic specimen.

A further quantity (0·95 g.) of the same compound was isolated in a similar manner from the material (1·75 g.) deposited by the acid extracts on cooling. In addition, these yielded a product (0·1 g., m. p. 130—135°), which was soluble in alkali and converted by treatment with methyl sulphate into the same ether. Evidently the product was 4-chloro-6-nitro-*m*-cresol. On diluting the cold acid extract with water, a precipitate (3·34 g.) was obtained, from which 4-chloro-6-nitro-*m*-toluidine (1·92 g., m. p. 120—121°) was isolated by extraction with benzene and crystallisation from alcohol. The base was identified by comparison with an authentic specimen, and by conversion into 4-chloro-2-nitrotoluene. A further quantity (0·3 g.) of the same amine was isolated from the crude base (0·49 g.) precipitated when the residual diluted acid liquor was rendered alkaline with ammonia. No pure material was furnished by the sticky substance (0·3 g.) obtained by extracting the alkaline filtrate with ether. In all the above cases, the end fractions were treated with acetic anhydride and acetyl chloride, but no definite acetyl derivatives were obtained, and it was assumed that the materials were azo- or azoxy-derivatives.

Action of Sodium Methoxide on 4-Chloro-2 : 5-dinitrotoluene.—When this compound (5 g.) had been heated for 2 hours at 100° with a solution of sodium (0·5 g.) in methyl alcohol (20 c.c.), the liquid was neutral and yielded 4-chloro-6-nitro-*m*-tolyl methyl ether (5·7 g.).

One of us (C. W. T.) expresses grateful acknowledgment of a grant from the Department of Scientific and Industrial Research which enabled him to participate in this work. Further, we wish to thank the Research Fund Committee of the Chemical Society for a grant towards the expenses of this investigation.

THE UNIVERSITY, SHEFFIELD. [*Received, August 10th,* 1925.]

CCCXX.—*The Formation of Chromones.—A Criticism.*

By WILSON BAKER.

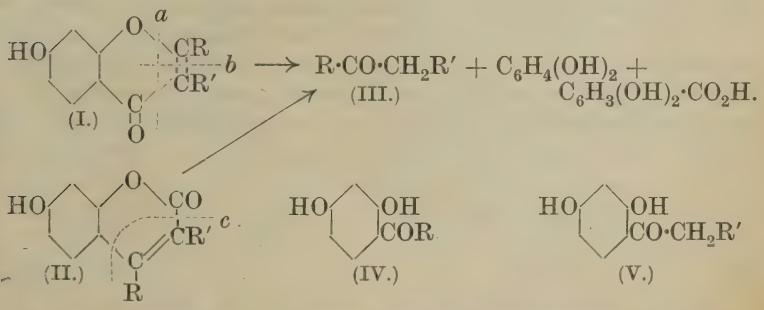
In a recent paper by Baker and Robinson (this vol., p. 1981) the view was put forward that the products described in a series of four papers on the synthesis of γ-benzopyrones or chromones (Jacobson and Ghosh, Parts I, II, and III, J., 1915, **107**, 424, 959, 1051; Ghosh, J., 1916, **109**, 106) are, in reality, the isomeric α-pyrones or coumarins, the substituent in position 2 of the chromones occupying position 4 in the coumarins. Since this criticism concerned twenty-four fundamental compounds and about

sixty derivatives thereof, it was considered desirable to investigate the subject further. A more detailed study has confirmed the view that all the products described in those papers are coumarins. no fewer than thirteen of the true chromones having now been prepared.

In the experiments described in the first three papers, substituted acetoacetic esters, $CH_3{\cdot}CO{\cdot}CHR{\cdot}CO_2Et$ (where R = benzyl, phenyl, or benzoyl), ethyl α-benzoyl-β-phenylpropionate, and ethyl α-phenylformylacetate were condensed with phenols usually in presence of concentrated sulphuric acid, but acetic acid and zinc chloride, or acetic acid and hydrogen chloride, were also used. In the cases of benzoylacetoacetic ester and ethyl acetylmalonate coumarins were admittedly produced. It is now clear that under such conditions coumarins are always formed, though it must be noted that with other condensing agents chromones may be produced. For example, Simonis and his collaborators have prepared chromone derivatives by condensing acetoacetic ester, and its methyl and ethyl derivatives, with phenols in presence of phosphoric anhydride (Petschek and Simonis, *Ber.*, 1913, **46**, 2015; Simonis and Lehmann, *Ber.*, 1914, **47**, 697; Simonis and Remmert, *ibid.*, p. 2229; see also Heilbron, Barnes, and Morton, J., 1923, **123**, 2569), the reaction being apparently of a general character.

In the fourth paper, nitriles of the type $R{\cdot}CHPh{\cdot}CN$ (where R = acetyl, formyl, or benzoyl) and benzoylacetonitrile were condensed with phenols usually in presence of sulphuric acid, but other condensing agents employed were acetic acid and hydrogen chloride, and phosphoryl chloride. The substances prepared from the nitriles corresponding to the carboxylic esters employed in the preceding papers were identical with the products prepared from those esters. Examination of the literature showed that it was exceedingly improbable that these condensations would produce chromones. For example, Meyer (*J. pr. Chem.*, 1903, **67**, 342) condensed benzoacetodinitrile, $NH{:}CPh{\cdot}CH_2{\cdot}CN$, with resorcinol in presence of concentrated sulphuric acid and obtained a product which was considered to be 7-hydroxyflavone, but which has subsequently been proved by Sonn (*Ber.*, 1918, **51**, 821) to be the isomeric 7-hydroxy-4-phenylcoumarin. Again, Bargellini and Forti-Forli (*Gazzetta*, 1911, **41**, i, 747) showed that by condensing *p*-methoxybenzoylacetonitrile and resorcinol by means of sulphuric acid, 7-hydroxy-4-*p*-methoxyphenylcoumarin is produced, and from the same nitrile Sonn (*loc. cit.*) has prepared 5 : 7-dihydroxy-4-*p*-methoxyphenylcoumarin (see also Sonn, *ibid.*, p. 1829). The present work has now fully established the fact that all such condensations of nitriles with phenols produce coumarins.

The constitutions of Ghosh's products were taken to be established by the fact that on hydrolysis with 33% or 50% aqueous potassium hydroxide they gave a neutral ketone, an *o*-hydroxy-acid, and in four cases (wherever it was sought) resorcinol; but in all, only five resorcinol derivatives were submitted to hydrolysis and these have all been definitely shown to be coumarins. The only other compounds submitted to hydrolysis were two derived from α-naphthol and one from *m*-cresol. The scheme given was as shown below, the supposed chromone (I) (really the isomeric coumarin II) undergoing hydrolysis along the dotted line *a*, giving the ketone (III), β-resorcylic acid, and resorcinol; whilst it was stated (Part I, *loc. cit.*, p. 427) that the complete hydrolysis of the coumarin (II) would produce the hydroxy-ketone (IV) and the acid $R'\cdot CH_2\cdot CO_2H$. But there seems very little experimental evidence to support such a method of fission, and it is shown below that the hydrolysis of coumarins, if it proceeds further than the mere opening of the pyrone ring, almost invariably takes quite another course. It is significant that in no case was a hydroxy-ketone of the type V produced, which is usually found as one of the products of alkaline decomposition of true chromones, owing to hydrolysis along the dotted line *b*.

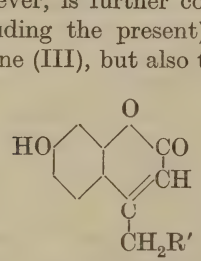


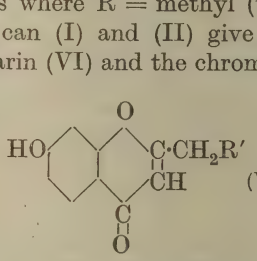
It follows that the production of the same neutral ketone is possible both from the chromone (I) and from the isomeric coumarin (II), owing, in the latter case, to hydrolysis along the line *c*. This is borne out by the fact that Jacobson and Ghosh's so-called 7-hydroxy-3-benzyl-2-methylbenzo-γ-pyrone (Part I, *loc. cit.*) (really 7-hydroxy-3-benzyl-4-methylbenzo-α-pyrone) gave on hydrolysis benzylacetone and β-resorcylic acid, whilst the true chromone (Crabtree and Robinson, J., 1918, **113**, 859) gave benzylacetone and benzylresacetophenone. It is seen, moreover, that the hydrolysis of (IV) along the line *c* accounts for the production of resorcinol, the formation of which is unsatisfactorily explained by Jacobson and Ghosh (J., 1915, **107**, 960) by assuming the decomposition of

β-resorcylic acid in presence of alkali. The method of production of β-resorcylic acid is not so obvious.

This course of hydrolysis of a coumarin appeared so novel that it was considered desirable to establish it beyond doubt. For this purpose the preparation and hydrolysis of Ghosh's so-called 7-hydroxy-3-phenyl-2-methylbenzo-γ-pyrone (which has since been proved to be 7-hydroxy-3-phenyl-4-methylbenzo-α-pyrone, Baker and Robinson, *loc. cit.*) were repeated, and the formation of benzyl methyl ketone (characterised by means of its semicarbazone and phenylhydrazone), resorcinol, and β-resorcylic acid was confirmed. From 3 g. of this coumarin were obtained about 0·5 g. of benzyl methyl ketone, a slightly smaller quantity of resorcinol, and only a very small amount of β-resorcylic acid, whilst some of the material was unhydrolysed. This confirms the view given above that the principal reaction is the production of benzyl methyl ketone and resorcinol, the β-resorcylic acid being only a by-product, and differs from Ghosh's view, that the chief reaction is the production of benzyl methyl ketone and β-resorcylic acid, the resorcinol being the by-product.

The important conclusion follows from these observations that the only safe criterion of the production of a chromone (I) and not the coumarin (II), is the formation on hydrolysis of a hydroxyketone (V), and shows the necessity for extreme caution in deciding the constitution of such substances by hydrolysis. The matter, however, is further complicated in cases where R = methyl (thus including the present), since not only can (I) and (II) give the ketone (III), but also the isomeric coumarin (VI) and the chromone

(VI.) 

 (VII.)

(VII). As proof of this, the compounds (I) and (VI), having R′ = phenyl (Baker and Robinson, *loc. cit.*), were submitted to hydrolysis under the conditions employed by Ghosh in the case of (II), the main results of which were verified as described above. Compound I underwent complete hydrolysis and gave a small amount of benzyl methyl ketone and about a 70% yield of 2 : 4-dihydroxyphenyl benzyl ketone; whilst compound VI, though incompletely hydrolysed, gave a relatively large yield of benzyl methyl ketone and resorcinol. The benzyl methyl ketone was in all cases characterised by means of its semicarbazone and phenylhydrazone, and the

melting points of mixtures of any of the specimens showed no depression. Compound VII (Hannach and Kostanecki, *Ber.*, 1902, **35**, 866) has not actually been hydrolysed under these conditions, but there is no doubt that it also would give benzyl methyl ketone as one of its fission products.

In the following paragraphs are given the correct properties of the compounds named and those of their derivatives, the first substance of each pair having previously been wrongly described by Jacobson and Ghosh and by Ghosh as the second. A comparison of the fluorescences of the two classes of compounds is not made, since both chromones and coumarins frequently show almost identical fluorescences under similar conditions.

The chromones described in this paper were prepared by the well-known reaction from ketones of the type V (where R′ = phenyl or benzyl) by acylation with a mixture of the anhydride and sodium salt of acetic or benzoic acid. Three of the necessary ketones (two previously unknown) were prepared by an application of the Hoesch synthesis.

Part I (*loc. cit.*): 7-Hydroxy-3-benzyl-4-methylbenzo-α-pyrone, m. p. 186°; acetyl derivative, m. p. 168°; methyl ether, m. p. 119°. 7-Hydroxy-3-benzyl-2-methylbenzo-γ-pyrone, m. p. 282°; acetyl derivative, m. p. 121°; methyl ether, m. p. 109° (Crabtree and Robinson, J., 1918, **113**, 867).

3-Benzyl-4 : 7-dimethylbenzo-α-pyrone, m. p. 117°. This preparation was originally carried out by Fries and Klostermann (*Annalen*, 1908, **362**, 27), and the correct constitution assigned to the compound.

7 : 8-Dihydroxy-3-benzyl-4-methylbenzo-α-pyrone, m. p. 185°; diacetyl derivative, m. p. 172°. 7 : 8-Dihydroxy-3-benzyl-2-methylbenzo-γ-pyrone, m. p. 203—205°; diacetyl derivative, m. p. 126° (this paper).

7-Hydroxy-3-benzyl-4 : 5-dimethylbenzo-α-pyrone, m. p. 177—178°; acetyl derivative, m. p. 169°. 7-Hydroxy-3-benzyl-2 : 5-dimethylbenzo-γ-pyrone, m. p. 294—295°; acetyl derivative, m. p. 138—139° (this paper).

5 : 7-Dihydroxy-3-benzyl-4-methylbenzo-α-pyrone, m. p. 218—219°; diacetyl derivative, m. p. 154°. 5 : 7-Dihydroxy-3-benzyl-2-methylbenzo-γ-pyrone, m. p. 200—201°; diacetyl derivative, m. p. 112° (this paper).

Part II (*loc. cit.*): 7-Hydroxy-3-benzyl-4-phenylbenzo-α-pyrone, m. p. 186°; acetyl derivative, m. p. 134°. 7-Hydroxy-3-benzyl-2-phenylbenzo-γ-pyrone, m. p. 272—274°; acetyl derivative, m. p. 150° (this paper).

7 : 8-Dihydroxy-3-benzyl-4-phenylbenzo-α-pyrone, m. p. 136—

137°; diacetyl derivative, m. p. 175°. 7 : 8-Dihydroxy-3-benzyl-2-phenylbenzo-γ-pyrone, m. p. 275—276°; diacetyl derivative, m. p. 175—176° (this paper).

5 : 7-Dihydroxy-3-benzyl-4-phenylbenzo-α-pyrone, m. p. 119°; diacetyl derivative, m. p. 56°. 5 : 7-Dihydroxy-3-benzyl-2-phenylbenzo-γ-pyrone, m. p. 202—203°; diacetyl derivative, m. p. 126° (this paper).

Part III (*loc. cit.*) : 7-Hydroxy-3-phenyl-4-methylbenzo-α-pyrone, m. p. 226°; acetyl derivative, m. p. 185°; methyl ether, m. p. 87°. 7-Hydroxy-3-phenyl-2-methylbenzo-γ-pyrone, m. p. 240°; acetyl derivative, m. p. 162°; methyl ether, m. p. 135·5° (Baker and Robinson, *loc. cit.*).

7 : 8-Dihydroxy-3-phenyl-4-methylbenzo-α-pyrone, m. p. 268°; diacetyl derivative, m. p. 211°. 7 : 8-Dihydroxy-3-phenyl-2-methylbenzo-γ-pyrone, m. p. 219—220°; diacetyl derivative, m. p. 115° (this paper).

5 : 7-Dihydroxy-3-phenyl-4-methylbenzo-α-pyrone, m. p. 178°; diacetyl derivative, m. p. 146°. 5 : 7-Dihydroxy-3-phenyl-2-methylbenzo-γ-pyrone, m. p. 228°; diacetyl derivative, m. p. 169° (Baker and Robinson, *loc. cit.*).

Ghosh (*loc. cit.*) : 7-Hydroxy-3-phenyl-4-methylbenzo-α-pyrone, identical with the product prepared in Part III.

7 : 8-Dihydroxy-3-phenyl-4-methylbenzo-α-pyrone, identical with the product prepared in Part III.

7-Hydroxy-3 : 4-diphenylbenzo-α-pyrone, m. p. 288°; acetyl derivative, m. p. 222°, and which on hydrolysis with 33% aqueous potassium hydroxide for 4 hours gave deoxybenzoin, resorcinol, and β-resorcylic acid. 7-Hydroxy-2 : 3-diphenylbenzo-γ-pyrone, m. p. 270—271°; acetyl derivative, m. p. 208—209° (Baker and Robinson, *loc. cit.*), and has now been found to give on hydrolysis under the above conditions a 93% yield of 2 : 4-dihydroxyphenyl benzyl ketone and benzoic acid.

7 : 8-Dihydroxy-3 : 4-diphenylbenzo-α-pyrone, m. p. 185°. 7 : 8-Dihydroxy-2 : 3-diphenylbenzo-γ-pyrone, m. p. 297° (this paper).

7-Hydroxy-4-phenylbenzo-α-pyrone, m. p. 243°. Ghosh's preparation has been repeated and a substance, m. p. 244°, obtained which crystallises, not in needles as stated, but in regular, four-sided plates having all the properties ascribed by Pechmann and Duisberg (*Ber.*, 1883, **16**, 2126) and Pechmann and Hancke (*Ber.*, 1901, **34**, 356) to 7-hydroxy-4-phenylbenzo-α-pyrone. Further, the melting point of a mixture with an authentic specimen of 7-hydroxy-2-phenylbenzo-γ-pyrone, m. p. 240°, kindly supplied by Mr. J. Allan (Allan and Robinson, J., 1924, **125**, 2192), showed a depression of about 30°.

Experimental.

Benzylresacetophenone.—A solution of β-phenylpropionitrile (10 g.) (Baker and Lapworth, J., 1924, **125**, 1334) and resorcinol (10 g.) in dry ether (75 c.c.) was saturated with dry hydrogen chloride at 0°. After 48 hours, water was added, the ether distilled off, and the ketimine hydrolysed by heating on the steam-bath for ½ hour. The oily product was extracted with chloroform, the solution shaken with aqueous sodium hydroxide, and the ketone liberated by acid. By recrystallisation from dilute acetic acid it was obtained in colourless needles, m. p. 88° (see Bargellini and Marantonio, *Gazzetta*, 1908, **38**, ii, 514).

7-*Hydroxy*-3-*benzyl*-2-*phenylbenzo*-γ-*pyrone.*—Benzylresacetophenone (5 g.), benzoic anhydride (20 g.), and anhydrous sodium benzoate (5 g.) were heated together at 170—180° for 6 hours. The product was hydrolysed by heating on the water-bath with alcohol (50 c.c.) and 50% aqueous potassium hydroxide (12 g. KOH) for 10 minutes, and the *pyrone* precipitated from the diluted solution by carbon dioxide. By recrystallisation from ethyl alcohol, in which it was sparingly soluble, it was obtained in small, colourless needles, m. p. 272—274° (Found : C, 80·3; H, 4·9. $C_{22}H_{16}O_3$ requires C, 80·5; H, 4·9%). Its colourless solution in aqueous sodium hydroxide shows a slight bluish-green fluorescence. The *benzoyl* derivative separates from alcohol in colourless, silky needles, m. p. 167°. The *acetyl* derivative, prepared by boiling with acetic anhydride for 6 hours and subsequently shaking with water, crystallises from alcohol in colourless prisms, m. p. 150° (Found : C, 77·8; H, 5·1. $C_{24}H_{18}O_4$ requires C, 77·8; H, 4·9%). The colourless solutions of these compounds in concentrated sulphuric acid show a weak blue fluorescence.

Benzylphloracetophenone.—A solution of β-phenylpropionitrile (15 g.) and anhydrous phloroglucinol (14·5 g.) in ether (100 c.c.) was saturated with hydrogen chloride at 0°. Hydrolysis of the ketimine was effected by heating with water on the steam-bath for ½ hour, the oily product dissolved by the addition of sodium hydroxide, the solution extracted with ether to remove non-phenolic substances, and the ketone liberated by a current of carbon dioxide and taken up with ether. Evaporation of the solvent left a pale yellow oil which solidified on stirring. It crystallised from hot water in colourless needles containing $1H_2O$ (Found : H_2O, 6·5. $C_{15}H_{14}O_4,H_2O$ requires H_2O, 6·5%), or in the anhydrous condition from chloroform in small prisms, m. p. 139—140° (Found : C, 69·7; H, 5·5. $C_{15}H_{14}O_4$ requires C, 69·7; H, 5·5%).

5 : 7-*Dihydroxy*-3-*benzyl*-2-*methylbenzo*-γ-*pyrone.*—A mixture of

anhydrous benzylphloracetophenone (2 g.), anhydrous sodium acetate (2 g.), and acetic anhydride (10 c.c.) was heated at 170—180° for 12 hours. After shaking with water, the *diacetyl* derivative was collected and recrystallised from alcohol, being obtained in colourless needles, m. p. 112° (Found : C, 68·9; H, 4·8. $C_{21}H_{18}O_6$ requires C, 68·8; H, 5·0%). The parent substance obtained by hydrolysis with boiling, dilute sodium carbonate solution and precipitation with acid, crystallised from dilute methyl alcohol in colourless, nacreous plates, m. p. 200—201° (Found : C, 72·1; H, 5·2. $C_{17}H_{14}O_4$ requires C, 72·3; H, 5·0%). Of its colourless solutions in aqueous sodium hydroxide and concentrated sulphuric acid, the latter only shows a weak blue-green fluorescence, which is also exhibited by a solution of the diacetyl derivative in the same solvent.

5 : 7-*Dihydroxy*-3-*benzyl*-2-*phenylbenzo*-γ-*pyrone*.—A mixture of benzylphloracetophenone (2 g.), benzoic anhydride (15 g.), and sodium benzoate (1 g.) was heated at 180—190° for 10 hours. The product was dissolved by heating on the steam-bath with a mixture of alcohol (50 c.c.) and water (5 c.c.), and hydrolysed by continuing to heat for 15 minutes with 50% aqueous potassium hydroxide (10 g. KOH); the product was precipitated from the diluted solution by carbon dioxide. By recrystallisation from methyl alcohol (charcoal) the *pyrone* was obtained in pale yellow prisms, m. p. 202—203°, containing methyl alcohol of crystallisation which is given up before melting (Found : C, 76·5; H, 4·8. $C_{22}H_{16}O_4$ requires C, 76·7; H, 4·7%). Its solution in aqueous sodium hydroxide shows no fluorescence. The *diacetyl* derivative, prepared by the action of acetic anhydride, crystallises from alcohol in pale yellow prisms, m. p. 126° (Found : C, 73·0; H, 4·6. $C_{26}H_{20}O_6$ requires C, 72·9; H, 4·7%). Both substances give pale yellow solutions in concentrated sulphuric acid which show very weak blue-green fluorescences.

Benzylorcacetophenone.—A solution of β-phenylpropionitrile (15 g.) and anhydrous orcinol (15 g.) in ether (100 c.c.) was saturated with hydrogen chloride at 0°. After 48 hours, the yellow crust of the ketimine was washed with ether and hydrolysed by heating on the steam-bath with water for ½ hour. The resulting oily ketone partly crystallised on standing for several days, consisting doubtless of a mixture of benzylorcacetophenone and the isomeric 2 : 6-dihydroxy-4-methylphenyl β-phenylethyl ketone. The product was pressed on porous earthenware, and the residue crystallised from a large volume of boiling water, shining, pearly plates, m. p. 118·5°, being obtained (Found : C, 75·1; H, 6·1. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3%). This ketone is proved to be benzylorcaceto-

phenone and not the isomeride by the fact that the benzo-γ-pyrone prepared from it has the properties of a 7- and not a 5-hydroxy-compound (see below).

7-*Hydroxy*-3-*benzyl*-2 : 5-*dimethylbenzo*-γ-*pyrone*.—The *acetyl* derivative obtained in the usual manner from benzylorcacetophenone by acetylation for 20 hours crystallised from methyl alcohol in colourless prisms, m. p. 138—139° (Found: C, 74·7; H, 5·7. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6%). The parent substance obtained by its hydrolysis with aqueous sodium carbonate crystallised from alcohol, in which it was sparingly soluble, in colourless needles, m. p. 294—295° (Found: C, 77·2; H, 5·9. $C_{20}H_{18}O_4$ requires C, 77·1; H, 5·8%). It dissolves readily in warm, dilute sodium hydroxide, giving a colourless solution showing a blue fluorescence. By methylation with methyl sulphate and potassium hydroxide at about 50°, it readily gave a *methyl* ether which crystallised from a small quantity of methyl alcohol in long, colourless prisms, m. p. 109°. All these substances give in concentrated sulphuric acid colourless solutions showing a blue fluorescence.

7 : 8-*Dihydroxy*-3-*phenyl*-2-*methylbenzo*-γ-*pyrone*.—Crude 2 : 3 : 4-trihydroxyphenyl benzyl ketone (10 g.; Noelting and Kadiera, *Ber.*, 1906, **39**, 2057) was acetylated in the usual manner for 24 hours. The oil obtained on treatment with water was extracted with ether, the extracts were shaken with aqueous sodium hydroxide to remove a small quantity of a phenolic substance, dried, and the ether was distilled, leaving a pale brown oil which rapidly crystallised. This *diacetyl* derivative is very readily soluble in the common organic solvents, but crystallises from a large volume of light petroleum (b. p. 60—80°) in colourless, silky needles, m. p. 111·5° (Found: C, 67·9; H, 4·4. $C_{20}H_{16}O_6$ requires C, 68·2; H, 4·6%). The parent substance obtained by its hydrolysis crystallises from dilute alcohol in thin, colourless prisms containing water of crystallisation which is readily given up at 100°. The anhydrous substance has m. p. 219—220° (Found: C, 71·3; H, 4·6. $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%).

7 : 8-*Dihydroxy*-2 : 3-*diphenylbenzo*-γ-*pyrone*.—This compound was prepared by benzoylation (20 hours) and subsequent hydrolysis of 2 : 3 : 4-trihydroxyphenyl benzyl ketone in the manner already described for the preparation of 5 : 7-dihydroxy-3-benzyl-2-phenylbenzo-γ-pyrone, and crystallised from alcohol in tiny, colourless needles, m. p. 297° (Found: C, 76·4; H, 4·1. $C_{21}H_{14}O_4$ requires C, 76·4; H, 4·3%). The *diacetyl* derivative crystallised from alcohol in fine, colourless, silky needles, m. p. 177—178° (Found: C, 72·2; H, 4·5. $C_{25}H_{18}O_6$ requires C, 72·4; H, 4·4%).

7 : 8-*Dihydroxy*-3-*benzyl*-2-*methylbenzo*-γ-*pyrone*.—Benzylgallaceto-

phenone (Dutta and Watson, J., 1912, **101**, 1241) was acetylated in the usual manner for 20 hours. The resulting *diacetyl* derivative crystallised from alcohol (charcoal) in almost colourless prisms, m. p. 126° (Found: C, 68·7; H, 4·9. $C_{21}H_{18}O_6$ requires C, 68·8; H, 5·0%). The parent substance obtained by its hydrolysis crystallised from very dilute alcohol in fine, colourless needles, which melt to a red liquid at 203—205° (Found: C, 72·0; H, 5·0. $C_{17}H_{14}O_4$ requires C, 72·3; H, 5·0%).

7 : 8-*Dihydroxy*-3-*benzyl*-2-*phenylbenzo*-γ-*pyrone* was prepared from benzylgallacetophenone in the same manner as the corresponding 2 : 3-diphenyl derivative described above. It crystallised from a large volume of acetic acid in pale yellow prisms, m. p. (when rapidly heated) 275—276° (Found: C, 76·4; H, 4·9. $C_{22}H_{16}O_4$ requires C, 76·7; H, 4·7%). This substance is very sparingly soluble in the usual organic solvents. The *diacetyl* derivative crystallises from alcohol in tiny, colourless, silky needles, m. p. 175—176° (Found: C, 72·6; H, 5·0. $C_{26}H_{20}O_6$ requires C, 72·9; H, 4·7%).

All these chromones derived from pyrogallol dissolve to pale yellow solutions in aqueous alkali hydroxides, none of which exhibits fluorescence (the same being true of the pale yellow solutions of the diacetyl derivatives in concentrated sulphuric acid); whilst their alcoholic solutions give a deep green colour with ferric chloride. The non-fluorescence of these substances is analogous to the cases of the *iso*brazilein and *iso*hæmatein salts and various benzopyrylium derivatives (Robinson, Crabtree, and Das, J., 1924, **125**, 211).

THE UNIVERSITY, MANCHESTER. [*Received, July 15th,* 1925.]

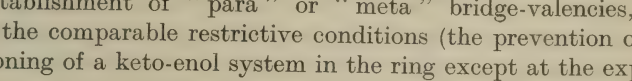
CCCXXI.—*The Formation and Stability of Associated Alicyclic Systems. Part II. The Formation and Disruption of Dicyclic Dihydroresorcinols.*

By ERNEST HAROLD FARMER and JOHN ROSS.

THE unsaturated cyclic ketones and ketonic esters of the five- and six-carbon series would appear to furnish attractive starting points for many chemical syntheses. In practice, however, owing to the transformations which accompany apparently simple operations, not only are the products other than those expected, but frequently it is extremely difficult to ascertain the course a given reaction has taken.

It has been recorded in the case of certain derivatives of dimethyl-*cyclo*pentenone (Farmer and Ingold, J., 1920, **117**, 1362; Farmer, Ingold, and Thorpe, J., 1922, **121**, 128) that the chemically active combination of double bond and carbonyl group may lead in cyclic

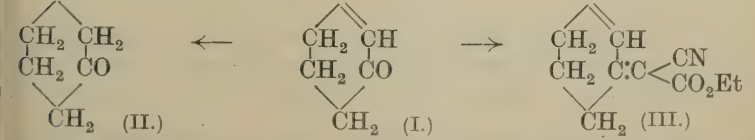
structures to a type of reactivity differing fundamentally from that observed in open-chain compounds, the effect of the spatial configuration and of the strained condition of the substituted carbon ring being such as to promote tautomeric valency exchange across the ring. Such a phenomenon might be expected to become manifest only under favourable structural and restrictive conditions, and, in the six-carbon series, where such an interchange would involve the establishment of "para" or "meta" bridge-valencies, and where the comparable restrictive conditions (the prevention of the functioning of a keto-enol system in the ring except at the expense



of valency adjustment across the ring) are exceedingly difficult of experimental realisation, no counterpart of the intra-annular tautomerism of the five-carbon series has yet been observed. In this connexion the uniplanar or multiplanar configuration is of moment; a multiplanar configuration, even although representing only changing contortions of the molecule and not giving rise to geometrical isomerides of the type obtained in the case of fused *cyclo*hexane rings (Hückel, *Nach. K. Ges. Wiss. Göttingen*, 1923, 43), would seem inevitably to affect intramolecular relationships.

In this series it is proposed to examine the relationships of the carbon pairs in a six-membered ring through their tendency to become united by bridges of one or more carbon atoms and in the present communication the ease of formation of 1 : 4-bridges consisting of the group $\cdot CH_2 \cdot CO \cdot$ is considered. The method employed is that of the Dieckmann condensation on the appropriate methyl-*cyclo*hexanone-acetic or -malonic esters.

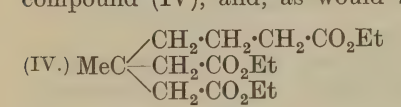
The mode of reaction between 1-methyl-Δ^1-*cyclo*hexen-3-one (I) and esters of the malonic type appears from the literature to be anomalous. Thus according to Rabe (*Ber.*, 1904, **37**, 1671) reaction between the ketone and ethyl sodioacetoacetate yields an additive product (II) of the Michael type, which subsequently undergoes an



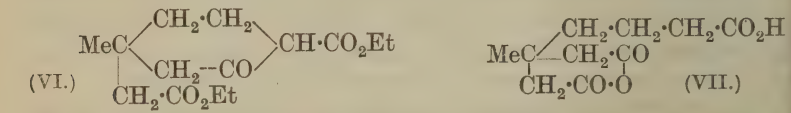
internal aldol condensation. With ethyl sodiocyanoacetate, however, it is stated (Knoevenagel and Mottek, *Ber.*, 1904, **37**, 4470) that reaction of the Knoevenagel type occurs leading to a methyl-

*cyclo*hexenylideneacetic ester (III), which also passes by internal condensation into a dicyclic compound.* Finally, towards ethyl sodiomalonate the ketone is stated to be indifferent (Vorländer and Gärtner, *Annalen*, 1898, **304**, 7).

Contrary to the last statement, ethyl sodiomalonate was found to react with the greatest facility, but the nature of the products varied with the experimental conditions used. When the condensation was effected at 100° in the presence of alcohol, the principal product was a high-boiling non-ketonic ester which, by reason of the difficulty attending its purification and that of its hydrolysis product, long resisted identification. It was ultimately identified as the compound (IV), and, as would be expected of such a substance,

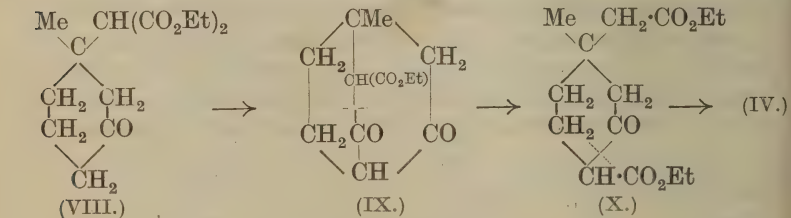


it yielded with sodium a cyclic keto-ester, presumably (VI), and its derived acid (V) an anhydro-acid, presumably (VII). The constitution of the tribasic acid (V) was finally established by synthesis



as recorded below, and the correctness of the formula assigned to the cyclic keto-ester (VI) followed from the subsequent oxidation of its derivatives.

The open-chain ester (IV) could have been produced only as the result of preliminary Michael addition followed in turn by internal condensation and two stages of ring fission, a procedure borne out

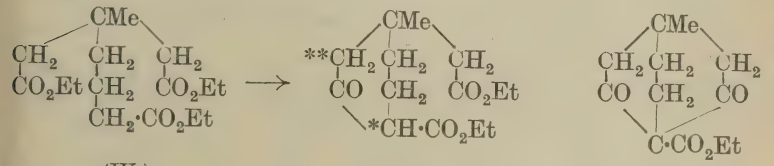


by the appearance of a quantity of the β-ketonic ester (X) along with the main product. In order to arrest the process before ring fission had occurred, the condensation was effected at room temperature.

* The alternative structures suggested for the dicyclic derivatives by Knoevenagel and Mottek involve internal condensations of such unusual type that the reinvestigation of the reaction between the cyclic ketone and ethyl cyanoacetate has been commenced.

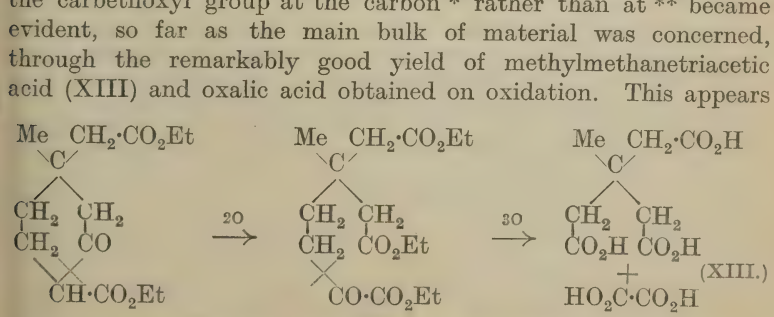
Among the products of reaction the original compound (VIII) and the open-chain ester (IV) could not be identified. Hydrolysis with mineral acids under special conditions gave a 50% yield of the methyl*cyclo*hexanoneacetic acid derived from (VI), but resinified the remainder of the material, regarded as representing the dicyclic 1 : 3-diketone (IX). The methyl*cyclo*hexanoneacetic acid produced was identical with that obtained by the direct condensation of β-methylpimelic-β-acetic ester (IV).

The attempted deliberate formation of the dicyclic diketone by the action of sodium on the ester (IV) failed so far as the main mass of material was concerned, the reaction proceeding only to the first stage (XI); nor could the pure ester (XI), derived from the acid (V), be converted into the dicyclic diketone.



(IV.) (XI.) (XII.)

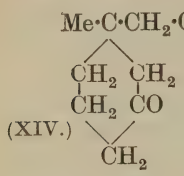
To the extent, however, of a few units per cent. there was obtained in the former reaction a crystalline quasi-acidic substance agreeing in composition with a dicyclodiketonic ester, but obtainable in insufficient amount to allow of the complete establishment of its constitution. The striking difference in the tendency towards further condensation of the esters (VIII) and (XI) may easily have arisen from the different distribution of the carbethoxyl groups. The non-formation in the latter case appears to have been due to the almost complete production of the *cis*-form of the monocyclic ester (XI) under the Dieckmann conditions, since the position of the carbethoxyl group at the carbon * rather than at ** became evident, so far as the main bulk of material was concerned, through the remarkably good yield of methylmethanetriacetic acid (XIII) and oxalic acid obtained on oxidation. This appears

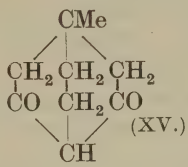


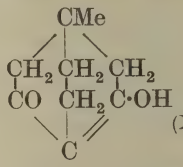
(XIII.)

the more probable in that the decarboxylated ester (XIV) reacted rapidly with sodium or even cold sodium ethoxide. Here, however,

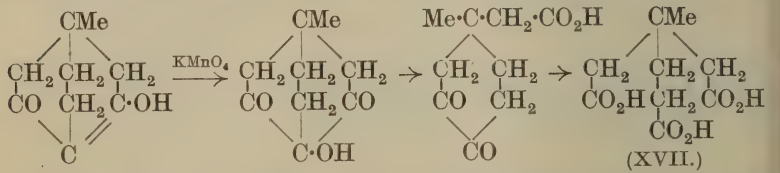
owing to the instability * and viscous nature of the product the type of condensation effected is as yet uncertain. Although not completely homogeneous, the product would appear from many of its properties (p. 2366) to consist essentially of the dicyclic dihydroresorcinol (XV or XVI). Thus on oxidation it gave good yields of


(XIV.)


(XV.)


(XVI.)

the expected tribasic acid (XVII) and was reconverted on prolonged boiling with caustic alkali into the acid corresponding to (XIV).

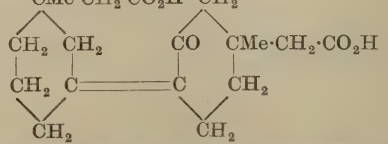

(XVII.)

Nevertheless, in the absence of crystalline derivatives and in view of the high values obtained for the molecular weight by the cryoscopic method, the possibility of intermolecular condensation of the Knoevenagel type having taken place is not ruled out.†

Of the three tribasic acids produced during this investigation, one, methylmethanetriacetic acid (XIII), had already been synthesised by Thorpe and Wood (J., 1913, **103**, 1583), and a specimen was obtained by repeating their synthesis. The two homologues of this acid (IV and XVII) were obtained from ethyl lævulate and ethyl γ-acetobutyrate, respectively, by means of the Guareschi method of synthesis. The ketonic esters gave with ethyl cyanoacetate and

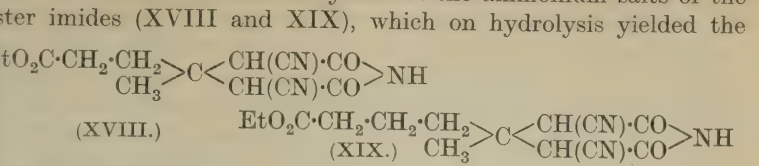
* The common dihydroresorcinols pass on attempted distillation into vitreous substances, and the only known dihydroresorcinol alkylated on the carbon between the carbonyl groups changes from a crystalline substance into a viscous oil on standing (Becker and Thorpe, J., 1922, **121**, 1303).

† Thus the compound of the annexed formula might be expected to yield (XVII) on oxidation and (XIV) on hydrolytic fission. On the other hand,



several undoubted examples of this type of condensation product have proved to be highly crystalline substances.

ammoniacal alcohol excellent yields of the ammonium salts of the ester imides (XVIII and XIX), which on hydrolysis yielded the



(XVIII.) (XIX.)

required acids (XVII and IV).

Experimental.

1-*Methyl*-Δ^1-cyclo*hexen*-3-*one*.—Large quantities of this ketone were prepared by the method of Rabe and Rahm (*Annalen*, 1904, **332**, 13), dilute sulphuric acid (10%) being used for the hydrolysis of the methylenediacetoacetic ester. In view of the subsequent withdrawal by Rabe (*Ber.*, 1912, **45**, 2924) of his earlier description of the properties of pure methyl*cyclo*hexenone, the purity of the product obtained was thoroughly tested by the quantitative degree of its conversion into the oxime and semicarbazone. The use of alkali as hydrolysing agent, as suggested in the later paper, proved far less satisfactory than that of sulphuric acid. After a preliminary fractionation in a vacuum, the portion distilling at 199—202° at the ordinary pressure (through a short column) could be regarded as pure ketone.

A. *Condensation of Ethyl Sodiomalonate with Methyl*cyclo*hexenone*.

(a) *At* 100°. The ketone (1 mol.) was gradually added to a cold alcoholic solution of ethyl sodiomalonate (1 mol.), and the mixture heated on a steam-bath for 16 hours. The cooled product was poured on to ice and separated in the usual way into three portions, which were respectively neutral, quasi-acidic (soluble in caustic alkali but insoluble in sodium carbonate), and acidic in reaction. The latter two fractions were red oils giving purple colours with ferric chloride. They represented less than 10% of the total material and could not be resolved into pure compounds.

Ethyl β-*Methylpimelate*-β-*acetate*.—The neutral portion (above) constituted over 90% of the reaction product. In the crude state it gave an intense blue colour with ferric chloride, but after exhaustive fractionation the material distilled constantly at 200°/18 mm. as a colourless oil, giving then a faint colour with ferric chloride. Only after hydrolysis and re-esterification of the acid produced, could the ester be obtained completely pure (Found: C, 60·6; H, 8·75. $C_{16}H_{18}O_6$ requires C, 60·7; H, 8·9%). The yield was 65% of the theoretical.

The remainder of the crude neutral portion (b. p. 180—185°/18

mm.) consisted principally of ethyl 1-methyl*cyclo*hexan-3-one-4-carboxylate-1-acetate (below).

β-*Methylpimelic*-β-*acetic Acid*.—The corresponding ester was boiled for 8 hours with 15% hydrochloric acid. After neutralising the solution with alkali and boiling off the alcohol, the acid was obtained in almost quantitative yield by ethereal extraction of the cooled, reacidified liquid. Evaporation of the ether left an oil which rapidly solidified. Complete purification of the acid for analytical purposes was a laborious process owing to the presence of a trace of a second substance which crystallised with the acid. This difficulty, which caused many months' delay in the original identification of the acid, was not experienced with the acid synthesised from γ-acetobutyric ester (p. 2368). Repeated crystallisation from acetone–chloroform and ethyl acetate yielded the acid in colourless prisms, m. p. 123—124° [Found: C, 52·0; H, 6·9; *M* (tribasic), 234. $C_{10}H_{16}O_6$ requires C, 51·7; H, 6·9%; *M*, 232]. On heating the acid for 1½ hours with excess of acetyl chloride, *anhydro*-β-*methylpimelic*-β-*acetic acid* (VII) was obtained. It crystallised from benzene in long, transparent needles, m. p. 83° (Found: C, 55·8; H, 6·4. $C_{10}H_{14}O_5$ requires C, 56·05; H, 6·6%).

The pure *ethyl* ester was prepared by saturating an alcoholic solution of the acid at 0° with dry hydrogen chloride and distilling the product in a vacuum. It was obtained in almost quantitative yield as a colourless oil, b. p. 200°/18 mm. (Found: C, 60·8; H, 9·15. Calc., C, 60·7; H, 8·9%).

(b) *At room temperature.* Since the ketone would not react appreciably with an alcohol-free, ethereal suspension of ethyl sodiomalonate, the condensation was effected as in (a) except that the mixture was not heated; it was kept in a closed vessel for a week. On working up the material, negligible quantities of quasi-acidic and acidic substances were obtained.

Ethyl 1-*Methyl*cyclo*hexan*-3-*one*-4-*carboxylate*-1-*acetate*.—The neutral ester so obtained (86% theory), although consisting largely of the methylcarboxy*cyclo*hexanone-acetic ester (VI), could not be satisfactorily resolved into its constituents. It was obtained on distillation as a colourless oil, b. p. 175—190°/16 mm. After repeated fractionation, specimens were obtained (b. p. 182°/16 mm.) which gave correct figures on analysis (Found: C, 62·2; H, 8·2. Required for $C_{14}H_{22}O_5$, C, 62·2; H, 8·2) for the carboxy-acetic ester (VI) or the isomeric ethyl 1-methyl*cyclo*hexan-3-one-1 malonate (VIII). The presence of the latter ester, however, could not be demonstrated and all fractions gave intense colours with ferric chloride. The pure ester was readily obtained by the method described below (p. 2366).

Ethyl Ethane-$^{1:2}$*II*$^{1:4}$*-1-methylcyclohexa-3 : 5-dione-2-carboxylate.** —Although this substance could not be isolated in pure condition from the condensation product, its presence was probably responsible for the considerable amount of resinous material obtained on hydrolysis of the ester mixture. Boiling with alcoholic sodium ethoxide converted the mixture into ethyl β-methylpimelate-β-acetate.

1-*Methylcyclohexan-3-one-1-acetic Acid.*—This substance was obtained in small amount from the ester fraction, b. p. 180—185°/18 mm., derived from the condensation effected at 100°, but in much larger quantities from the product of condensation at 15°. The ester, after one distillation, was boiled with a mixture of equal volumes of alcohol and concentrated hydrochloric acid diluted with 2 volumes of water. After boiling for 3 hours, the excess of alcohol was expelled and refluxing continued for a further 7 hours. The cooled product was neutralised with sodium carbonate and extracted with ether. The mother-liquor was acidified with hydrochloric acid and re-extracted with ether. The oil thus isolated, on distillation, was obtained pure and colourless; b. p. 196°/15 mm., yield 60%. The acid passed on standing for some weeks into a solid, m. p. 37°. The *semicarbazone* was formed with considerable difficulty and did not crystallise well, thus rendering purification difficult. It separated from methyl alcohol as a white powder, m. p. 189° (Found: C, 52·2; H, 7·5. $C_{10}H_{17}O_3N_3$ requires C, 52·8; H, 7·5%). The *silver* salt was obtained as a white powder (Found: Ag, 38·8. $C_9H_{13}O_3Ag$ requires Ag, 39·0%).

Ethyl 1-methylcyclohexan-3-one-1-acetate was obtained by treatment of the silver salt of the acid with alcoholic ethyl iodide. It was a colourless oil, b. p. 147°/15 mm., which yielded no colour with ferric chloride (Found: C, 66·5; H, 9·2. $C_{11}H_{18}O_3$ requires C, 66·6; H, 9·15%). The ester could readily be converted into its *semicarbazone*, which separated from ether in colourless prisms, m. p. 158—159° (Found: C, 56·2; H, 8·2. $C_{12}H_{21}O_3N_3$ requires C, 56·4; H, 8·3%).

B. *Direct Condensation by the Dieckmann Method.*

General Method.—Sodium (2 atoms) was pulverised under xylene and the xylene replaced by a volume of benzene or toluene equal to that of the ester (1 mol.), which was immediately added. The whole was heated on a steam-bath until energetic reaction commenced. When this had subsided, heating was re-commenced and continued

* The nomenclature used for this and succeeding dicyclic compounds is that described in Part I of this series (J., 1920, **117**, 591).

until reaction was complete. The cooled product was treated with ice and extracted with ether. The mother-liquor was then acidified and extracted.

Intramolecular Condensation of Ethyl β-*Methylpimelate*-β-*acetate*.—The neutral ester obtained in 75% yield by the general method distilled as a colourless oil (b. p. 182°/15 mm.) which gave a deep purple colour with ferric chloride. This was pure *ethyl* 1-*methyl*-cyclo*hexan*-3-*one*-4-*carboxylate*-1-*acetate* (p. 2364) (Found: C, 61·9; H, 8·3. $C_{14}H_{20}O_5$ requires C, 62·2; H, 8·2%). This ester yielded no semicarbazone, but on hydrolysis by the method recorded above (p. 2365) yielded an acid identical in all respects (including the properties of its derivatives) with the methyl*cyclo*hexanoneacetic acid previously described. From the silver salt the ethyl ester (semicarbazone, m. p. 158—159°) was readily prepared. For the preparation of large quantities of this ester the foregoing method, in conjunction with the Guareschi synthesis (below), is especially suitable.

Ethyl Ethane-$^{1:2}$II$^{1:4}$-1-*methyl*cyclo*hexa*-3 : 5-*dione*-2-*carboxylate*.—The portion of the condensation product which was soluble in caustic alkali but insoluble in sodium carbonate was distilled (b. p. 190—200°/18 mm.). The distillate deposited crystals which on recrystallisation from light petroleum were obtained in long, colourless needles, m. p. 111°. This substance did not immediately give a colour with ferric chloride; an intense colour developed after 10 minutes (Found: C, 63·7; H, 7·4. $C_{12}H_{16}O_4$ requires C, 64·1; H, 7·1%). Owing to the small amount of material available, the correctness of the constitution assigned could not be fully established.

Ethyl Hydrogen 1-*Methyl*cyclo*hexan*-3-*one*-4-*carboxylate*-3-*acetate*.—The acidic portion of the condensation product partly solidified. By treatment with ligroin the separation of the solid from the oily matter was possible. On recrystallisation from ligroin, the solid melted at 91° and gave an immediate colour with ferric chloride (Found: C, 59·4; H, 7·55. $C_{12}H_{18}O_5$ requires C, 59·5; H, 7·5%). Hydrolysis of the crude acid fraction gave a good yield of methylpimelic-acetic acid.

Intramolecular Condensation of Ethyl 1-*Methyl*cyclo*hexan*-3-*one*-1-*acetate*.—The small amount of neutral ester derived by condensing the cyclic ester (XI) with sodium according to the general method proved to be unchanged material. The large amount of acidic material was almost entirely soluble in sodium carbonate and gave no colour with ferric chloride. On distillation in a vacuum a portion passed over as a viscous, colourless oil (containing some methyl-*cyclo*hexanoneacetic acid), but the major portion would not distil

and set to a resinous mass on cooling. The undistilled substance readily gave a silver salt which on treatment with methyl iodide yielded an oil, only a portion of which passed over on distillation and from which no pure substance could be obtained. Numerous attempts to purify the acidic substance were without success, nor could crystalline derivatives be obtained. The composition and basicity corresponded approximately with that of *ethane*-$^{1:2}$II$^{1:4}$-1-*methyl*-Δ^3-cyclo*hexen*-3-*ol*-5-*one* (XVI). A similar product was obtained by using alcoholic sodium ethoxide instead of sodium. This material, after prolonged desiccation, gave in benzene solution molecular weight values almost double of that corresponding to formula XV or XVI. Boiling for some hours with caustic soda caused conversion into methyl*cyclo*hexanoneacetic acid.

C. *Oxidation of Cyclic Compounds.*

Oxidation of Ethyl 1-*Methyl*cyclo*hexan*-3-*one*-4-*carboxylate*-1-*acetate*.—To an ice-cold suspension of the ester in very dilute caustic potash, 3% potassium permanganate solution equivalent to about 5 atoms of oxygen was added drop by drop, with rapid stirring. After removal of the manganese, the solution was evaporated to small bulk and extracted with ether. From the concentrated ethereal solution an excellent yield of a sand-coloured acid separated. This was methylmethanetriacetic acid, which, after precipitation from concentrated aqueous solution by hydrogen chloride and finally crystallising from acetone–chloroform, separated in colourless prisms, m. p. 172° [Found: C, 46·8; H, 6·0; *M* (tribasic), 210. Calc., C, 47·0; H, 5·9%; *M*, 204]. This acid was compared directly with the acid synthesised by Thorpe and Wood's method (*loc. cit.*) and found to be identical.

From the aqueous mother-liquor an amount of calcium oxalate approximately equivalent to the organic acid was isolated.

Oxidation of the Product of Reaction of Sodium on Ethyl 1-*Methyl*-cyclo*hexan*-3-*one*-1-*acetate*.—The substance, dissolved in dilute sodium carbonate, was oxidised under conditions very similar to those described above. The intermediate oxidation products possessed considerable stability and the solution needed stirring for 1½ hours after addition of the necessary amount of permanganate (corresponding to 3 atoms of oxygen) was complete. After filtering and concentrating, the solution was acidified with hydrochloric acid. The intense bright red colour thus produced persisted for several days, but was instantly discharged by ammonia, only to reappear on acidification with acetic acid. Extraction of the acid liquor with ether yielded an oil which slowly deposited a crystalline acid.

This separated in small, colourless prisms, m. p. 148—149°, from acetone–chloroform [Found : C, 49·3; H, 6·55; *M* (tribasic), 212. $C_9H_{14}O_6$ requires C, 49·5; H, 6·5%; *M*, 218]. This acid was compared directly with a specimen synthesised from ethyl lævulate (Section D) and found to be identical.

D. *Guareschi Synthesis of Polycarboxylic Acids.*

β-*Methylpimelic*-β-*acetic Acid.*—Ethyl γ-acetobutyrate (8 g.), prepared by Bentley and Perkin's method (J., 1896, **69**, 1511), was mixed with ethyl cyanoacetate (11·3 g.). To the cold mixture, ammoniacal alcohol (25 c.c.) saturated at −10° was added. The product was kept at 0° in a tightly stoppered bottle for 2 days; inoculation with a crystal of an analogous imide then initiated crystallisation. Thus the ammonium salt (m. p. 97°) of an ester imide was obtained in good yield. From this the imide separated on acidification as a thick oil which soon solidified. More of the imide was obtained from the mother-liquor by removing the alcohol, without applying heat, and acidifying. It separated from dilute aqueous alcohol in long, transparent needles, m. p. 138—139° (Found : C, 57·3; H, 5·8; N, 14·9. $C_{14}H_{17}O_4N_3$ requires C, 57·7; H, 5·9; N, 14·4%).

The imide (2·5 g.) was mixed with 15 c.c. of concentrated sulphuric acid; when water (15 c.c.) was added, the imide dissolved. After 7 hours' boiling, hydrolysis was complete without carbonisation having taken place. Ethereal extraction of the cooled, diluted product yielded an oily acid which soon solidified in an evacuated desiccator (yield 2·1 g.). Recrystallisation from concentrated acetone–chloroform solution yielded colourless, well-defined prisms of β-methylpimelic-β-acetic acid, m. p. 124—125°. This m. p., differing by 1° from that recorded above, was not depressed by admixture of the two acids [Found : C, 51·7; H, 7·1; *M* (tribasic), 234. Calc., C, 51·7; H, 6·9%; *M*, 232].

β-*Methyladipic*-β-*acetic Acid.*—This acid was prepared from ethyl lævulate analogously to the preceding one. The crystalline ammonium salt (m. p. 136°) gave an excellent yield of the ester imide (XVIII), which separated from aqueous alcohol in long, transparent needles, m. p. 169° (Found : C, 55·6; H, 5·5; N, 15·8. Required for $C_{13}H_{15}O_4N_3$, C, 56·3; H, 5·4; N, 15·2%).

By hydrolysis of the imide with a mixture of equal volumes of sulphuric acid and water the acid was obtained. It was recrystallised from a mixture of equal volumes of acetone and chloroform, from which it separated in hard, colourless prisms, m. p. 148—149° (Found : C, 49·35; H, 6·4. Calc., C, 49·5; H, 6·5%).

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CCCXXII.—*Applications of Thallium Compounds in Organic Chemistry. Part II. Titrations.*

By GEORGE HALLATT CHRISTIE and ROBERT CHARLES MENZIES.

AMONG new salts prepared by titration (see, *inter alia*, Menzies and Wilkins, J., 1924, **125**, 1148) are *thallous fumarate* and *thallous maleate*, which exhibit differences in properties similar to those displayed by the acids.

Tetrathallium tartrate, $C_4H_2O_6Tl_4$, prepared in alkaline solution, is sparingly soluble in water; the solution turns phenolphthalein pink, and the amount of acid required to discharge the colour corresponds to two equivalents of thallium. The salt may be recrystallised unchanged from a sufficiency of water; if, however, carbon dioxide be passed while heating, solution takes place more rapidly and the liquid on cooling deposits the characteristic needles of thallous carbonate. These facts indicate that two of the four thallium atoms are hydrolysable.

This salt does not appear to have been prepared before, as thallous tartrate has hitherto been made from the acid and thallous carbonate (Kuhlmann, *Compt. rend.*, 1862, **55**, 608; Carstanjen, *J. pr. Chem.*, 1867, **102**, 146; Lamy and des Cloizeaux, *Ann. Chim. Phys.*, 1869, **17**, 335; Glucksmann, *Z. Kryst. Min.*, 1894, **23**, 566). Carstanjen states that thallous tartrate has an alkaline reaction, but we find that tartaric acid may be accurately titrated with thallous hydroxide solution and phenolphthalein, the end-point being sharp.

In its somewhat sparing solubility, tetrathallium tartrate resembles the double tartrate of thallium and antimony (Kuhlmann; Lamy and des Cloizeaux; *loc. cit.*), and it is possible that it is the first example of a metallic hydroxy-acid complex formed by a univalent metal (see Wark, J., 1923, **123**, 1815).

An attempt to prepare tetrapotassium tartrate failed, normal potassium tartrate alone being obtained by concentration of a solution containing potassium hydroxide (4 equivs.) and tartaric acid (1 equiv.). Thallium compounds prepared on similar lines from lactic, malic, citric, and salicylic acids gave irregular analytical

results. β-Diketones, however, and phenols give thallium salts which resemble tetrathallium tartrate in the ease with which they can be prepared pure, and in the accuracy with which the thallium, hydrolysed by water, may be estimated by titration. These compounds are now described, as the usefulness of readily prepared, well-crystallised substances of this type is obvious. The crystalline forms are often characteristic and develop on mixing drops of the solutions, so that their possible application in micro-analysis is indicated. Of interest are the *thallous* salts of ethyl acetoacetate and of benzoylacetone, which resemble the thallous salts of acetylacetone and of acetonedicarboxylic ester in being readily soluble in organic solvents. Reactions of the above types of compound are under investigation and will be described in a later communication. Diphenyl ether, for instance, is formed by refluxing a solution of thallous phenoxide in iodobenzene, *o*-methoxybenzaldehyde has been obtained in 62% yield by heating thallium salicylaldehyde (Menzies and Wilkins, *loc. cit.*) under reflux with methyl iodide in benzene, and methyl stearate in quantitative yield from thallous stearate in the same way. The latter reactions as well as the former show that the resemblance between univalent thallium and the metals of both the A and the B sub-group of group 1 of the periodic table is not confined to inorganic chemistry.

Experimental.

Thallous Salts of Organic Acids.—These salts were prepared by titrating the acids with standardised thallous hydroxide solution and phenolphthalein, and were analysed after being filtered off and dried in a vacuum at 100°. The accuracy of the titrations is the same as in the cases of sodium and potassium hydroxides, the values for the equivalent weights of the acids generally being correct to three significant figures.

Thallous fumarate separates, when the solution obtained by titration is cooled, in white, elongated prisms, m. p. 268° (decomp.) (Found: Tl, 77·9. $C_4H_2O_4Tl_2$ requires Tl, 78·2%). It is sparingly soluble in water. *Thallous maleate* crystallises, on evaporation of its solution over sulphuric acid, in thick, white prisms, m. p. 164—166° (Found: Tl, 77·85. $C_4H_2O_4Tl_2$ requires Tl, 78·2%). It is readily soluble in water. *Thallous succinate* crystallises in irregular plates, m. p. 246—248°, on slow evaporation of its solution (Found: Tl, 77·6. $C_4H_4O_4Tl_2$ requires Tl, 77·9%). *Thallous phthalate* forms white prisms, m. p. 268—270° (Found: Tl, 70·8, 71·1. $C_6H_4O_4Tl_2$ requires Tl, 71·4%).

Holde and Selim (*Ber.*, 1925, **58**, 524) prepared thallous palmitate and oleate (Menzies and Wilkins, *loc. cit.*) and thallous stearate by

titrating alcoholic solutions of the acids with $N/10$-aqueous thallous hydroxide and recrystallising the precipitated salts from alcohol. By the use of Kahlbaum's purified acids and a more concentrated solution of thallous hydroxide the pure salts may be obtained in one operation as follows: 7·35 g. of stearic, 8·96 g. of palmitic, and 9·76 g. of oleic acid, each dissolved in 200 c.c. of warm alcohol, required 29·9 c.c., 40·43 c.c., and 39·9 c.c. of 0·864N-aqueous thallous hydroxide (theory, 29·95, 40·48, and 40·03 c.c. respectively). On concentration and cooling there were obtained 10 g. of thallous stearate (m. p. 119°), 14 g. of thallous palmitate (m. p. 115°), and 8 g. of thallous oleate (m. p. 78—82°) (Found: Tl, 42·1 for oleate, 41·55 for stearate, 44·3 for palmitate. Calc., Tl, 42·1, 41·9, 44·5% respectively).

The observation that thallous palmitate softens at 116—118° but does not melt completely at 170° (Menzies and Wilkins, *loc. cit.*, p. 1149) led to its examination by polarised light * between crossed nicols; it was then found that between the above temperatures the salt behaves as an anisotropic liquid. The stearate and oleate show similar changes (see Holde and Selim, *loc. cit.*).

The thallous tartrate obtained by slow evaporation of its solution prepared by titration was dried in air (Found: on drying in a vacuum for 2 hours at 100—110°, H_2O, 1·6; in dried salt, Tl, 73·2. Calc. for the hemihydrate,† H_2O, 1·6; for the dried salt, Tl, 73·4%). This salt has a neutral reaction when redissolved in water. The salt obtained by Carstanjen (*loc. cit.*), and described as having an alkaline reaction, contained according to his analysis a slight excess of thallium (73·74%); both observations point to contamination with thallous carbonate used in its preparation.

Tetrathallium tartrate is deposited whenever a solution containing tartaric acid and thallous thallium is made alkaline. (1) 12·5 G. (78% of the theoretical yield) were obtained from 2·5 g. of tartaric acid and four equivalents of thallous hydroxide solution (121·4 c.c. of approximately 0·55N), the first few drops of which in excess

* At the suggestion of Professor Lapworth.

† 2-Methylpyridine-3 : 4 : 6-tricarboxylic acid (Lawson, Robinson, and Perkin, J., 1924, **125**, 637) forms another of the few thallous salts containing water of crystallisation. 7·8 G. (theory 8·7) of the above salt were obtained from 2·35 g. of the acid (kindly supplied by Professor Robinson) as a white, crystalline powder which, on heating, charred without melting. After exposure to moist air to constant weight, it lost on subsequent heating at 140—145° 1·9% of its original weight. Another sample, dried to constant weight at 145°, gained 2·2% of its final weight on exposure to moist air till the weight was again constant (6 days) [Found in dried salt: Tl, 73·1 (as Tl1), 73·2 (as Tl_2O_3). $C_6H_4ON_6Tl_3$ requires Tl, 73·4%. $C_9H_4ON_6Tl_3,H_2O$ requires H_2O, 2·1%]. By a coincidence, 2-methylpyridine-3 : 4 : 6-tricarboxylic acid and tartaric acid have the same equivalent weight.

produced a precipitate (Found: Tl, 84·2 as iodide, 42·5 by titration.* $C_4H_2O_6Tl_4$ requires Tl, 84·8%). (2) 5·86 G. (yield 87·6%, calculated on thallous hydroxide taken) were obtained from 1·77 g. of acid potassium tartrate and three times the amount of thallous hydroxide solution required to neutralise the salt (Found by titration: Tl, 42·55%). (3) 37 G. (yield 77%) were obtained from a hot solution of 7·5 g. of tartaric acid, 8 g. of sodium hydroxide, and 50·4 g. of thallous sulphate in 500 c.c. of water (Found: Tl, 84·7, 84·8 as iodide; 42·5, 42·8% by titration). (4) 3·2 G. were obtained from 6 g. of normal thallous tartrate hemihydrate and 50 c.c. of approximately 0·44*N*-sodium hydroxide solution (Found by titration: Tl, 42·3%). (5) 0·38 G. was obtained from 1·39 g. of thallium hydrogen tartrate and 27 c.c. of the same sodium hydroxide solution (Found by titration: Tl, 42·5%).

Decomposition by carbon dioxide. Tetrathallium tartrate (9·9 g.) only partly dissolved in 50 c.c. of boiling water; but on passing carbon dioxide dissolution was rapid and, on cooling, 3·7 g. of thallous carbonate crystallised. Hydrolysis of half the thallium with formation of carbonate requires 4·8 g. of thallous carbonate, which is appreciably soluble in water.

Comparative Estimations, by Titration and by Precipitation as Thallous Iodide, of Thallium in its Salts with β-Diketones and with Phenols.—Thallous ethyl acetoacetate. The pure *compound* (24·3 g.) separated in needles, m. p. 91—92°, when 100 c.c. of thallous hydroxide solution (27·5 g. of TlOH per 100 c.c.) were mixed with 16·2 g. of ethyl acetoacetate dissolved in a little alcohol. The substance is readily soluble in organic solvents (Found: Tl, 61·1 as iodide; 61·2 by titration. $C_9H_9O_3Tl$ requires Tl, 61·3%).

The thallous salt of benzoylacetone (6·3 g.) was obtained in long, yellow prisms, m. p. 103—105°, from 7·3 g. of benzoylacetone and the equivalent amount of thallous hydroxide solution. It is sparingly soluble in pure ether, but conveniently recrystallised from acetone (Found: Tl, 55·9 as iodide; 55·6 by titration. $C_{10}H_9O_2Tl$ requires Tl, 55·9%).

Thallous acetyl acetone (Kurowski, *Ber.*, 1910, **43**, 1078; Morgan and Moss, J., 1914, **105**, 195). Found: Tl, 67·0 as iodide; 66·9 by titration. Calc., Tl, 67·4%.

The thallous salt of acetonedicarboxylic ester (Menzies and Wilkins, *loc. cit.*). Found: Tl, 49·85 as iodide; 50·0 by titration. Calc., Tl, 50·5%.

Thallous salts of phenols. Pure thallous phenoxide, m. p. 231—

* Percentages of thallium given as "by titration" have been calculated on the basis of 0·02044 g. of thallium per c.c. of *N*/10-acid required to neutralise weighed amounts of the substances in question in aqueous solution.

235° (Kuhlmann, *Bull. Soc. chim.*, 1864, **1**, 333), crystallises in long needles on cooling the solution obtained by mixing equivalent weights of phenol in alcohol and of thallous hydroxide in hot water. Supersaturation occasionally occurs (Found: Tl, 69·1 as iodide: 68·7 by titration. Calc., Tl, 68·7%).

Thallous m-*tolyloxide*, m. p. 187°, crystallises pure when a hot solution of *m*-cresol in an equivalent quantity of aqueous thallous hydroxide is cooled [Found: Tl, 65·2 as iodide; 65·7 by titration (methyl-orange). C_7H_7OTl requires Tl, 65·6%].

o- and *p*-Cresol also give characteristic salts, that of *o*-cresol differing from the others in its greater solubility in water.

The thallous salt of resorcinol monomethyl ether (2·48 g.) was obtained in thin prisms, m. p. 146—148°, from 1·28 g. of resorcinol monomethyl ether and 8·1 c.c. of 1·27 *N*-thallous hydroxide solution (yield 73·5%) [Found: Tl, 62·25, 62·4 as iodide; 63·0 by titration (methyl-orange). $C_7H_7O_2Tl$ requires Tl, 62·4%].

The thallous salt of guaiacol (8·1 g.) was obtained from 5·7 g. of guaiacol and 36·1 c.c. of 1·27*N*-thallous hydroxide solution in stout, rhombohedral plates, m. p. 160—161° (yield 53·7%). This salt is much less soluble in water than the salt of resorcinol monomethyl ether (Found: Tl, 62·4, 62·25 as iodide; 63·0% by titration).

Thallous α-*naphthoxide*, m. p. 180—190°. On cooling a hot aqueous solution of this substance, obtained in the usual way as an amorphous precipitate, an emulsion was first produced which, examined by ordinary light under a microscope, appeared to consist of small globules suspended in the liquid. These were invisible in plane-polarised light between crossed nicols, crystals of stout, doubly refracting plates soon crystallised and the emulsion disappeared [Found: Tl, 58·25 as iodide; 58·6 by titration (methyl-orange). $C_{10}H_7OTl$ requires Tl, 58·8%].

The thallous salt of vanillin separates in branching needles, m. p. 193—201°, in almost theoretical yield when a weighed amount of vanillin, dissolved in a little alcohol, is added to an equivalent quantity of moderately concentrated thallous hydroxide solution (Found: Tl, 56·8, 57·0 as iodide; 57·0 by titration. $C_8H_7O_3Tl$ requires Tl, 57·5%).

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CCCXXIII.—*The Reactions of Azoxy-compounds. Part I. The Action of Light.*

By William Murdoch Cumming and George Straton Ferrier.

Although much has been published on the preparation of azoxy-compounds, few attempts have been made to explore the reactions of this somewhat stable group. Scattered observations (notably by Knipscheer, *Rec. trav. chim.*, 1903, **22**, 1) indicate that one characteristic reaction of azoxy-compounds, their conversion into hydroxyazo-compounds under the influence of sulphuric acid, can also be brought about by the action of light. Knipscheer obtained *o*-hydroxyazobenzene, in poor yield (10·3%), and with much loss of material through volatilisation (39·7%), by exposing sheets of filter-paper impregnated with azoxybenzene to sunlight for 5 weeks. He further stated, as a result of experiments in boiling benzene and toluene, that the transformation took place satisfactorily only when the azoxybenzene was in the solid state. As this did not agree with observations made in this laboratory (Cumming and Steel, J., 1923, **123**, 2465; Cumming and Ferrier, J., 1924, **125**, 1108) on αα′- and ββ′-azoxynaphthalenes, and as it was further believed that the loss of azoxybenzene through volatilisation could be greatly reduced by carrying out the transformation in solution, it was decided to reinvestigate the subject.

By exposing solutions of azoxybenzene in various solvents to the light of a mercury vapour lamp, *o*-hydroxyazobenzene was obtained in fair yield, varying with the conditions. The best results (28·0%) for 50 hours' exposure were obtained in absolute ethyl alcohol, and the worst (7·7%) in benzene. Increase of temperature materially increased the loss of azoxybenzene through volatilisation, and only slightly improved the yield. The transformation also takes place in sunlight, but cannot be effected by ordinary electric light. In this connexion it is of interest that Cumming and Steel (*loc. cit.*) have found that exposure of αα′-azoxynaphthalene to sunlight or to the light of a mercury vapour lamp for a short period produced a red isomeride of the same melting point (127°); prolonged exposure, however, produced an azonaphthol melting at 224° (private communication). This change they formulate thus:

$$\underset{\text{Yellow azoxynaphthalene.}}{\text{R·N(O)–N·R}} \longrightarrow \underset{\text{Red isomeride.}}{\text{R·N(O):N·R}} \longrightarrow \underset{\text{Azonaphthol.}}{\text{R·N:N·R·OH}}$$

We have also obtained hydroxyazo-compounds from 2 : 2′-, 3 : 3′-, and 4 : 4′-azoxytoluenes, 4 : 4′-dichloroazoxybenzene, and

2 : 2′-diamino-4 : 4′-azoxytoluene under similar conditions. 4 : 4′-Azoxyanisole, 4 : 4′-azoxyphenetole, and 4 : 4′-dinitroazoxybenzene reacted slightly or not at all. In the case of 2 : 2′-azoxytoluene products of widely different melting points were obtained according to whether the transformation was carried out in alcohol or benzene solution. The hydroxyazo-compounds were obtained as red needles of varying solubility in sodium hydroxide solution. In cases where we were able to determine the orientation, the hydroxyl group appears to enter the benzene nucleus in the ortho-position with respect to the azo-group.

Janovsky and Reimann (*Ber.*, 1889, **22**, 40, 1172) state that by fractionally crystallising the product from the action of zinc and sodium hydroxide on *p*-nitrotoluene they obtained an isomeric *p*-azoxytoluene melting at 75°, which they state can also be obtained by the oxidation of *p*-azotoluene with nitric acid. We have been unable to obtain this isomeride by either method, and have shown that it is not a solid solution of *p*-azo- in *p*-azoxy-toluene. Our work, therefore, indicates that the existence of this isomeride is extremely doubtful.

Experimental.

Azoxybenzene.—A. *Effect of ultra-violet light.* Azoxybenzene (5 g.), dissolved in 85% alcohol (500 c.c.) contained in a quartz flask and placed under a reflux condenser to reduce loss through volatilisation, was exposed for 50 hours to the light of a mercury vapour lamp. The alcohol was then distilled off and the red, crystalline residue dissolved in ether and exhaustively extracted with 8% sodium hydroxide solution (2 litres). The ethereal solution after extraction yielded 3·65 g. of azoxybenzene. The alkaline extract, after acidification with hydrochloric acid, was kept overnight and filtered. A yellow powder (1·05 g.), m. p. 76—78°, was obtained, which was completely volatile in steam (hence containing no *p*-hydroxyazobenzene) and after crystallisation from alcohol formed red needles, m. p. 82—83°. Bamberger (*Ber.*, 1900, **33**, 1939) gives for *o*-hydroxyazobenzene m. p. 82·5—83°.

The compound was further characterised by formation of the copper salt described by Bamberger, who does not, however, give details of the method for its preparation. This can best be accomplished by mixing equivalent quantities of an alcoholic solution of cupric chloride with a sodium ethoxide solution of the dyestuff, and leaving to crystallise. The salt melted at 223° (Bamberger gives m. p. 225—226°).

A control experiment was carried out by keeping a similar solution of azoxybenzene in the dark for 14 days and working up

similarly. Pure azoxybenzene was recovered quantitatively. A sample of *o*-hydroxyazobenzene in alcoholic solution was exposed to the lamp for 125 hours, and the product fractionally crystallised from alcohol. No change was apparent.

The yields (per cent. of *o*-hydroxyazobenzene after 50 hours' illumination) obtained with various solvents were : 85% EtOH, 20·5; 100% EtOH, 28·0; MeOH, 24; PrOH, 26·3; C_6H_6, 7·7; boiling 85% EtOH, 22·3.

Dilution of the 85% ethyl-alcoholic solution from 1% to 0·5% of the azoxy-compound left the yield practically unaltered (26·0, 24·6%), but increase of time of exposure to 100 and 200 hours raised the yield to 44·0% and 63·3% respectively.

B. *Action of sunlight.* On June 24th, 1924, a solution of 18 g. of azoxybenzene in 1300 c.c. of 85% alcohol was divided between (i) a quartz flask (500 c.c.), (ii) a glass flask of approximately the same dimensions as (i) but with thinner walls (500 c.c.), and (iii) a thick glass reagent bottle (300 c.c.), in the proportions indicated. The flasks having been corked, and luted with sealing wax, were clamped to a retort stand in such a way as to ensure equal illumination, and exposed on the roof of the College until September 24th, when they were taken in and worked up in a similar manner to the other experiments. From the solution in (i) were obtained 1·56 g. (31·2%); from the solution in (ii), 1·88 g. (37·2%); and from the solution in (iii), 1·00 g. (33·3%), of the hydroxyazo-compound. Further experiment showed, however, that when the light of a mercury vapour lamp was employed, a solution in glass was only one-half as much transformed as one in quartz.

C. *Action of electric light.* A metal-filament lamp was immersed in a solution of 7·5 g. of azoxybenzene in 750 c.c. of alcohol, and lit for 50 hours. The solution had then only slightly changed colour, and on working up yielded pure azoxybenzene quantitatively.

2 : 2′-*Azoxytoluene.*—2 : 2′-Azoxytoluene (3 g.), dissolved in 85% alcohol (300 c.c.) and illuminated for 50 hours by means of the mercury vapour lamp, on transference to ethereal solution and extraction with 8% sodium hydroxide yielded practically nothing. The ether was removed, and the red, crystalline product added to a solution of 5 g. of 2 : 2′-azoxytoluene in alcohol, also previously illuminated. The whole was then fractionally crystallised from alcohol. The less soluble fractions were identified as 2 : 2′-azoxytoluene, the more soluble ones after purification and distillation under reduced pressure (b. p. 164°/3 mm.) melted at 47·5—48·5° and formed orange-red needles giving a deep-red solution in alcohol (Found : N, 12·4. $C_{14}H_{14}ON_2$ requires N, 12·4%).

Sixteen grams of 2 : 2′-azoxytoluene were dissolved in 650 c.c.

of benzene and illuminated for 50 hours. The solution, which had turned deep red, was concentrated, and extracted with 8% sodium hydroxide solution, to which it yielded nothing. After removing the benzene, and shaking with sodium hydroxide solution for 3 days (with negative results), the product was fractionally crystallised from alcohol. Together with unaltered initial material, a very small amount of red needles, m. p. 92—93°, closely resembling in appearance the other hydroxyazo-compounds, was obtained, but not in sufficient quantity for analysis.

3 : 3′-*Azoxytoluene.*—This substance was prepared by the method of Buchka and Schachteback (*Ber.*, 1889, **22**, 834), with slight modification. The purification of the azoxy-compound from traces of the nitro-compound sufficient to prevent crystallisation proved difficult, but the following procedure gave satisfactory results. The reduction mixture was steam-distilled, and the residue extracted with ether. After removal of as much of the ether as possible by distillation, the product was taken up in absolute alcohol and the last traces of ether were removed by heating on the water-bath. On dilution with a few drops of water and cooling in a freezing mixture, crystals of 3 : 3′-azoxytoluene separated. Further purification by crystallisation from 85% alcohol presented no difficulty.

Two flasks containing, respectively, 5 g. and 1·55 g. of 3 : 3′-azoxytoluene dissolved in 500 c.c. of 85% alcohol were illuminated for 52 hours. On working up as in the case of azoxybenzene, 0·38 and 0·17 g. respectively were obtained of a yellow powder, which after recrystallisation from alcohol formed red needles, m. p. 61·5—62·5° (Found : N, 12·6. $C_{14}H_{14}ON_2$ requires N, 12·4%). 4-Hydroxy-3 : 3′-dimethylazobenzene melts at 115°, and 6-hydroxy-3 : 3′-dimethylazobenzene at 95°. Therefore this substance is probably *2-hydroxy-3 : 3′-dimethylazobenzene.*

4 : 4′-*Azoxytoluene.*—*Preparation* : see p. 2378.

Action of light. 4 : 4′-Azoxytoluene (4·72 g.), dissolved in 85% alcohol (500 c.c.) and illuminated for 54 hours, was treated as in the case of azoxybenzene, 6 litres of 8% sodium hydroxide solution being necessary to complete the extraction. 3-Hydroxy-4 : 4′-azoxytoluene (yield 0·47 g., or 10%), m. p. 150—151°, and otherwise agreeing with Macpherson and Boord's description (*J. Amer. Chem. Soc.*, 1911, **33**, 1531), was obtained.

4 : 4′-*Azoxyanisole.*—4 : 4′-Azoxyanisole (4·34 g.), dissolved in alcohol (500 c.c.), was illuminated for 50 hours, the solution being kept boiling to retain the azoxy-compound in solution. On cooling, 3·21 g. of pure azoxyanisole separated out (m. p. after recrystallisation 116·7°, clearing point 134°). The united mother-liquors

were evaporated, and the residues dissolved in ether and extracted with 1·litre of 16% sodium hydroxide solution. An orange, alkaline extract was obtained, which turned red on acidification, depositing a minute crop of red crystals, melting after crystallisation at 121°, but in too small quantity for further examination. On evaporation of the ethereal solution a further quantity (0·5 g.) of *p*-azoxyanisole was obtained.

In a previous experiment a curious effect was observed whereby a solution which had been illuminated for 17 hours became deep green, almost black. On illumination for a further period of 11 hours this colour faded to orange.

4 : 4′-*Dichloroazoxybenzene*.—4 : 4′-Dichloroazoxybenzene (5 g.) dissolved in boiling 85% alcohol was illuminated for 50 hours at the boiling point. After working up in the usual way, making use of sodium hydroxide solution, a small yield of red crystals, m. p. 171—172°, was obtained (Found: N, 9·8. $C_{12}H_8ON_2Cl_2$ requires N, 9·5%).

2 : 2′-*Diamino*-4 : 4′-*azoxytoluene*.—Three solutions were illuminated, a 1% solution in alcohol, a solution of the hydrochloride in water, and a similar solution in water containing excess of hydrochloric acid. In each case the product was much contaminated with tar. After removal of this by boiling alcoholic solutions with animal charcoal, and fractionally crystallising from alcohol, small quantities of red needles, m. p. 210°, were obtained. Graeff (*Annalen*, 1885, **229**, 346) gives for a hydroxyazotoluidine obtained by the action of sulphuric acid on 2 : 2′-diamino-4 : 4′-azoxytoluene a melting point 212°.

Reported Isomerism of 4 : 4′-*Azoxytoluene*.—Samples of 4 : 4′-azoxy- and azo-toluene were prepared from *p*-nitrotoluene by the method of reduction by zinc dust and ammonium chloride applied by us to other nitro-compounds (Cumming and Steel, Cumming and Ferrier, *loc. cit.*). Exhaustive fractional crystallisations from acetic acid and from absolute alcohol of the mixtures of azoxy- and azo-toluene obtained gave no trace of any compound melting at or about 75°. Further experiments in which the method of reduction employed by Janovsky was followed in detail were similarly unsuccessful. The yield from the former reduction is 10% better than from the latter. The action of 3 parts of nitric acid (*d* 1·51) does not, in our hands, give a product melting at 75°, but a mixture of a red substance, m. p. 202°, probably tetranitroazotoluene (Janovsky, *Monatsh.*, 1888, **9**, 839), with a white substance, m. p. 153°. The formation of the latter is favoured by increase of time of nitration. As it was suspected that the substance melting at 75° might be a solid solution of azotoluene in azoxytoluene

(compare Hartley and Stuart, J., 1914, **105**, 309, for the case of azobenzene and azoxybenzene), a setting-point curve of mixtures of *p*-azo- and *p*-azoxy-toluene was prepared. This revealed, however, no irregularities. From the setting point, 69·95°, of the pure azoxy-compound, the curve rises fairly steeply to the point corresponding to 75° and 10% of the azo-compound; addition of azotoluene to the azoxy-compound, therefore, does not depress the setting point of the latter. The curve then rises, first with slight concavity (relative to the composition axis) to the point corresponding to 140° and 99% of the azo-compound, and then steeply to 143·4°, the setting point of the pure azo-compound. A 50% mixture has a setting point of 118·5°.

It is a pleasant duty for one of us (G. S. F.) to acknowledge his indebtedness to Messrs. Nobel Industries and to the Carnegie Trustees for scholarships during the tenure of which this work was carried out.

ROYAL TECHNICAL COLLEGE, GLASGOW. [*Received, July 6th*, 1925.]

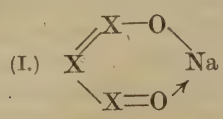
CCCXXIV.—*Co-ordinated Compounds of the Alkali Metals. Part II.**

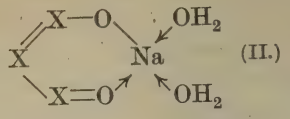
By NEVIL VINCENT SIDGWICK and FREDERICK MASON BREWER.

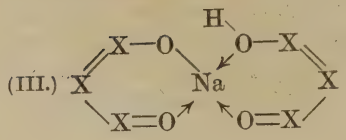
THE discovery by Plant (*loc. cit.*) of the 4-covalent alkaline derivatives of ψ-indoxyl*spirocyclo*pentane made it of interest to see whether such derivatives were formed by the simpler compounds which give chelate rings with multivalent metals, such as β-diketones, β-ketonic esters, *o*-hydroxy-aromatic esters and aldehydes, and *o*-nitrophenols, the alkaline derivatives of which have hitherto been regarded as salts. It is possible that in some cases they are not salts, but covalent compounds with the metal forming part of a chelate ring (type I) as the replaceable hydrogen does in the original compound (Sidgwick and Callow, J., 1924, **125**, 532; Sidgwick, this vol., p. 907). The metallic atom might also assume a higher covalency of 4 or 6 (especially of 4, which is in general very stable); but it can only do so by forming addition compounds, either with the original or some similar organic compound, as happens with the ψ-indoxyl derivatives (III), or possibly by the co-ordination of two single molecules, as for example of water (II). Finally a third chelate ring

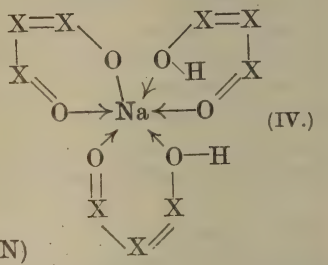
* Part I: Sidgwick and Plant, this vol., p. 209.

might be added in the same way, giving a 6-covalent metallic atom (IV).









(X = C or N)

It will be seen from what follows that there is considerable evidence for the existence of substances of the first of these types, and we have prepared numerous examples of the second and third, and some of the fourth.

1. *Simple Alkaline Derivatives.*

The alkaline derivative of, say, a β-diketone may either be a salt, or may have the metal covalently attached to oxygen. From the strong tendency of the alkali metals to ionise, we should not expect the compound to be covalent unless this made a further increase of stability possible, as through the closing of a chelate ring, which can happen with these compounds. Hence the alternative structures are (1) a salt and (2) a 2-covalent chelate compound. In the first case, the substance will have the usual properties of the salt of an organic acid: it will be insoluble in non-hydroxylic solvents and soluble in water, and on heating it is likely to decompose (char) without melting. In the second case, we may expect non-polar properties; a definite melting point, and greater solubility in organic solvents than in water.

The examination of the alkaline derivatives of substances of this kind shows that their properties are sometimes those of polar and sometimes those of non-polar compounds. They can behave in one of three ways, as the following examples show.

(1) When a benzene solution of ethyl malonate is treated with sodium, the sodium derivative separates as it is formed; it is quite insoluble in benzene, and when heated it chars without melting: it behaves as a salt.

(2) If ethyl methylmalonate is used, the sodium dissolves to form a clear solution, from which the compound does not immediately

separate even on concentration; but when once it has separated it is quite insoluble in benzene or toluene. (This might be ascribed to the formation of a colloidal solution, but the gradation of properties as we pass from class 1 to class 3 makes this improbable.)

(3) If ethyl acetoacetate is used, the sodium compound is found to melt to a clear liquid at 108°, and to be quite soluble in hot toluene.

These differences in behaviour suggest that the members of class 1 are always salts; that those of class 2 are non-polar chelate compounds when first produced, but on separation change into a more stable ionised form; whilst those of class 3 are stable in the non-polar form.

From our own observations and those recorded in the literature it appears that the majority of these compounds are of the first class. All the lithium derivatives we have prepared (including those of acetoacetic ester, acetylacetone, benzoylacetone, *o*-nitrophenol, 3-nitro-*o*-cresol, and quinizarin) are of this kind; they are insoluble in toluene and decompose on heating without fusion. Of the sodium derivatives, those of ethyl malonate, acetylacetone, ethyl cyanoacetate, methyl salicylate, salicylaldehyde, *o*-nitrophenol, 3-nitro-*o*-cresol, and quinizarin belong to this class. On the other hand, the sodium derivatives of the alkyl- and phenyl-malonic esters and (according to unpublished results of Dr. A. F. Titley) of 1-ketohydrindene-2-carboxylic ester, behave like that of methylmalonic ester (class 2), and the sodium salt of ethyl picrylmalonate (Jackson and Soch, *J. Amer. Chem. Soc.*, 1896, **18**, 133) does not separate on formation, although it is only very slightly soluble in benzene.

The sodium derivatives of acetoacetic ester, of ethyl ethylacetoacetate (Wislicenus, *Ber.*, 1874, **7**, 683), and of ethyl ethanetetracarboxylate belong to the third class, and are moderately soluble in non-hydroxylic solvents.

Of the comparatively few potassium derivatives examined, those of ethyl acetoacetate, ethyl cyanoacetate, and benzoylacetone are soluble to some extent in benzene and toluene, and melt at 106°, 135—137° and 146°, respectively, so that they belong to the third class. Where the sodium compounds are of the second kind, their potassium analogues appear to behave as salts (class I), and to be insoluble in benzene.

It is to be noticed that the replacement of the hydrogen attached to the middle carbon atom of the three (as in the esters of the alkylmalonic acids) promotes the stability of the non-polar form: this may be connected with its effect (on the Thorpe–Ingold theory) in closing up the chelate group.

There is thus some evidence of the existence of chelate compounds of 2-covalent sodium and potassium.

2. 4- *and* 6-*Covalent Derivatives* (*Addition Compounds*).

Many of these metallic derivatives which are insoluble in benzene and toluene readily dissolve in those solvents in presence of excess of the mother-substance. Thus it was found that sodium ethyl malonate, though quite insoluble in benzene, easily dissolved on warming in benzene containing an excess of malonic ester. On further heating, a gelatinous precipitate separated, consisting of the sodiomalonate. This suggests that a soluble addition compound is formed, which dissociates on heating. Evaporation of the solvent in the cold left a pasty mass from which no definite compound could be isolated. Similar behaviour was observed with ethyl methylmalonate, ethyl cyanoacetate, acetylacetone, benzoylacetone, and ethyl acetoacetate, though no precipitation took place on heating. It is not necessary that the parent substance should be present; for example, sodium acetylacetone will dissolve in a benzene solution of acetoacetic ester.

The more definite salts, such as the sodium derivatives of *o*-nitrophenol, salicylaldehyde, methyl salicylate, and the oximes of benzil, did not dissolve in benzene solutions of the parent substance, but were soluble in the parent substance itself. The solid obtained by the action of powdered sodium on excess of methyl salicylate, after drying on a porous plate, melted at 144° and contained 7·8% of sodium ($C_8H_7O_3Na$,$C_8H_8O_3$ requires Na, 7·2%), but on washing with ether it lost ester continuously; it may therefore be only a mixture, but is more probably an unstable compound. An analogous compound of salicylic acid, $C_7H_5O_3Na$,$C_7H_6O_3$, has been described by Hoitsema (*Z. physikal. Chem.*, 1898, **27**, 312): this we found not to be soluble as a whole in organic solvents: on prolonged treatment with benzene or ether it slowly lost salicylic acid, leaving a residue of sodium salicylate.

An attempt was made to prove the formation of a compound in solution by observing the depression of the freezing point of a solution of acetoacetic ester in benzene on addition of the sodium derivative; if the latter were wholly combined, its addition would cause no further depression. The available concentrations were limited by the separation of the sodium compound or of gelatinous products, but the results given in the following table indicate that some combination takes place, although it is by no means complete; the calculated values of the depression caused by the sodium compound are on the assumption that no combination occurs.

Per Cent. Ester	6·42	6·43	6·40	9·06	11·57
F. p. Depression	2·42°	2·42°	2·61°	3·62°	4·37°
Per Cent. Na Deriv.	2·56	1·52	0·872	0·828	0·585
Further Depression: Calc.	0·90°	0·53°	0·31°	0·29°	0·20°
Further Depression: Obs.	0·23°	0·18°	0·10°	0·10°	0·02°

Attempts to establish the formation of these compounds by means of solubility curves of the sodium derivative in the ester, either alone or in presence of toluene, were vitiated by the decomposition of the sodium derivative and its reaction with the ester at the temperatures required.

These facts taken together render it very probable that sodium is capable of forming 4-covalent compounds with substances of this kind; but for a definite proof the isolation of the products is needed.

Preparation of 4-Covalent Compounds.

Derivatives of Benzoylacetone.—The sodium derivative of benzoylacetone, $C_6H_5\cdot C(ONa):CH\cdot CO\cdot CH_3$, behaves as a salt: it has no definite melting point, and is quite insoluble in hydrocarbons. On recrystallisation from 96% alcohol, however, it became easily soluble in toluene. Analysis showed that the compound had taken up two molecules of water from the aqueous alcohol (Found: C, 54·2; H, 5·4; Na, 10·2. $C_{10}H_9O_2Na,2H_2O$ requires C, 54·55; H, 5·9; Na, 10·5%). It melts at 115°, with some preliminary loss of water; the water was identified by its b. p., and by its action on anhydrous copper sulphate. It is somewhat soluble in benzene and chloroform The solubility in hydrocarbons is in marked contrast to the behaviour of the original sodium derivative, and clearly shows that the compound is not a hydrated salt. The closure of the chelate ring is evidently due to the possibility of securing, by means of the water molecules, a stable covalency of 4 (formula II). The 96% alcohol contains just enough water to form the hydrate, but not enough to hydrolyse the original salt; on recrystallisation from water a small amount of the hydrate was obtained, but the greater part of the compound was hydrolysed. It was not found possible to prepare a double compound of sodium benzoylacetone and benzoylacetone; if water was carefully excluded, no product was obtained, and if water was present, the hydrate was formed.

A corresponding lithium compound was obtained, but it could not be freed from anhydrous salt (which is much less soluble in alcohol than its sodium analogue) by recrystallisation from alcohol. It was recrystallised from ethyl acetate, in which it is readily soluble (the anhydrous salt is insoluble). It forms lustrous, pearly plates (Found: Li, 3·4. $C_{10}H_9O_2Li,2H_2O$ requires Li, 3·4%).

Potassium benzoylacetone, which melts at 146° and is somewhat soluble in toluene, does not appear to form a stable hydrate.

Acetoacetic Ester.—A hydrate of the sodium derivative was prepared by Elion (*Rec. trav. chim.*, 1884, **3**, 240); by adding the ester to a suspension of excess of powdered sodium hydroxide in ether (in complete absence of moisture) he obtained a solution of the sodium derivative

in ether (presumably containing a non-polar compound with the ether), from which the hydrate was precipitated on adding a few drops of water. He describes this as a monohydrate, but his analyses are not very accurate. We found that it is very difficult to avoid the simultaneous precipitation of the anhydrous form, while the hydrate itself is very unstable. A freshly prepared specimen, precipitated by very vigorous stirring with a slight excess of water, melted at 102° and was completely soluble in benzene (the anhydrous salt melts at 108° and is practically insoluble in benzene, although it dissolves in hot toluene) (Found: C, 38·6; H, 6·2; Na, 12·75. $C_6H_9O_3Na,2H_2O$ requires C, 38·3; H, 6·6; Na, 12·2%). Although not quite pure, the compound is evidently the dihydrate. On standing, it decomposes, finally giving a substance of m. p. 82°, insoluble in benzene, which is also obtained by adding excess of water to Elion's solution of the sodium derivative; from its analysis it appears to be the dihydrate of sodium acetoacetate (Found: C, 31·0; H, 6·1; Na, 14·5. $C_4H_5O_3Na,2H_2O$ requires C, 30·0; H, 5·6; Na, 14·4%). This is confirmed by the fact that whilst the aqueous solution of the original dihydrate when acidified becomes turbid (from separation of ester), that of this product remains clear but evolves carbon dioxide. De Forcrand (*Ann. Chim.*, 1895, **5**, 405) obtained similar results. In the same way, Thorpe (J., 1900, **77**, 923) found that an aqueous solution of the sodium derivative of cyanoacetic ester is converted on evaporation to dryness into sodium cyanoacetate without any intermediate alkaline reaction. It is probable that the chelate form of the ester hydrate hydrolyses directly to the chelate isomeride of the salt hydrate.

Acetylacetone.—The sodium derivative was converted by recrystallisation from aqueous alcohol, acetone, or ethyl acetate into a hydrate; pearly plates, giving off water on heating, soluble in ethyl acetate (in which the anhydrous compound is insoluble), but not soluble in toluene. Very unstable: a specimen recrystallised from alcohol and ethyl acetate gave C, 35·8; H, 6·8; Na, 14·1; another specimen gave Na, 14·5 ($C_5H_7O_2Na,2H_2O$ requires C, 38·0; H, 7·0; Na, 14·55%). The potassium derivative is similar (Found: K, 23·0. $C_5H_7O_2K,2H_2O$ requires K, 22·4%); it rapidly decomposes, being apparently hydrolysed by its own water.

No lithium compound could be prepared.

Methyl Salicylate.—Only the lithium derivative forms a stable hydrate, produced on crystallisation from aqueous alcohol; it separates in plates, soluble in ethyl acetate (from which they were recrystallised) and in toluene (Found: Li, 3·8. $C_8H_7O_3Li,2H_2O$ requires Li, 3·6%). On heating, it loses water gradually, and finally melts at about 278°.

Salicylaldehyde.—Lithium compound. A solution of lithium hydroxide added to the aldehyde immediately precipitates the yellow, crystalline dihydrate: glistening, yellow plates (from alcohol), soluble in toluene, forming a colourless solution (Found: C, 50·5; H, 5·3; Li, 4·4. $C_7H_5O_2Li,2H_2O$ requires C, 51·2; H, 5·5; Li, 4·3%). It gives off water on heating, and melts indefinitely at about 228°.

Sodium compound. Hantzsch (*Ber.*, 1906, **39**, 3089) found that even with excess of sodium ethoxide salicylaldehyde forms an "acid salt"—an addition product of a molecule of the aldehyde and one of the simple salt. We found that this compound on washing with warm solvents gradually reverts to the simple salt (Found: Na, 15·9. $C_7H_5O_2Na$ requires Na, 16·0%); but by washing with cold ether it could be obtained pure (Found: Na, 8·7. $C_7H_5O_2Na,C_7H_6O_2$ requires Na, 8·6%); the same compound (Found: Na, 8·8%) separates from an alcoholic solution of the simple sodium salt to which an excess of the aldehyde has been added.

Potassium ethoxide was found by Hantzsch to behave in the same way, except that excess of it destroys the complex.

These double compounds are yellow, crystalline substances, slightly soluble in toluene, forming yellow solutions (the simple sodium and potassium derivatives are insoluble in toluene); they dissociate on heating in the solid state, and also in solution except in presence of excess of the aldehyde. Thus among the salicylic derivatives it is only with lithium that the monochelate hydrated form is produced; the sodium and potassium salts of the aldehyde give the dichelate form (formula III), corresponding to the ψ-indoxyl compounds. These differences no doubt depend on the relation between the strain in the ring and the size of the metallic atom.

o-*Nitrophenol.*—The ease with which salicylaldehyde forms chelate addition products with its salts suggested that it might do so also with other similar alkaline salts, such as those of the nitrophenols; and this was found to be so. The bright red sodium *o*-nitrophenoxide is a definite salt, soluble in water and hot alcohol, insoluble in toluene or ether. If salicylaldehyde is added to the solid salt the red colour at once disappears, the aldehyde is absorbed, and a bright yellow substance produced. After washing with ether, this has the composition of an addition compound of the salt and the aldehyde (Found: Na, 8·4. $C_6H_4O_3NNa,C_7H_6O_2$ requires Na, 8·1%). It dissolves in toluene on warming to form a yellow solution, which on further heating loses its colour and deposits the red sodium *o*-nitrophenoxide; excess of aldehyde prevents this dissociation. The same change occurs on heating the dry solid. No similar compound is formed from sodium *p*-nitrophenoxide. The substance evidently has the dichelate structure (III).

When sodium *o*-nitrophenoxide is crystallised from alcohol containing excess of salicylaldehyde, yellow, feathery crystals separate, mainly consisting of this substance, but with rather a high sodium content (9·3%) owing to some sodium salicylaldehyde and free nitrophenol having been formed: the latter has no tendency to form an addition compound, and remains in solution.

The yellow compound cannot be a mixture of nitrophenol and sodium salicylaldehyde, since its composition does not change on washing with ether.

Lithium forms no corresponding compound; the yellow crystals which were produced were found to be impure dihydrate of lithium salicylaldehyde.

Potassium *o*-nitrophenoxide in the anhydrous state is red, but it easily takes up water to form an orange hydrate, $2C_6H_4O_3NK,H_2O$ (Fritzsche, *Annalen*, 1859, **110**, 153; Frazer, *Amer. Chem. J.*, 1903, **30**, 309). This hydrate is slightly soluble in toluene, in which the red salt is quite insoluble. Either form yields with salicylaldehyde an ochre-yellow compound which is difficult to purify. When freshly made, it contained 13·8% of metal ($C_6H_4O_3NK,C_7H_6O_2$ requires K, 13·0%); it rapidly became discoloured, and after recrystallisation from alcohol contained excess of potassium, owing, no doubt, to interaction between the aldehyde and the salt.

3-*Nitro*-o-*cresol*.—This gave very similar results. The dry sodium salt changed from red to yellow on addition of salicylaldehyde, and the product after washing and drying gave Na 7·4% ($C_7H_6O_3NNa,C_7H_6O_2$ requires Na, 7·7%). The potassium salt absorbed a large excess of the aldehyde (possibly forming a 6-covalent derivative), but no definite compound could be isolated. When the lithium salt of the nitrocresol was recrystallised from an alcoholic solution of the aldehyde, only the dihydrate of lithium salicylaldehyde was obtained.

When acetylacetone was substituted for salicylaldehyde, no substance of this type was produced; either no reaction took place, or the alkaline salt of acetylacetone was formed.

Quinzarin.—The derivatives of 1-hydroxyanthraquinone can form chelate rings with the multivalent metals of the same type as those given by the β-diketones, and their lakes are recognised as chelate compounds (Werner, Morgan). Quinizarin (1 : 4-dihydroxyanthraquinone) was selected as having each hydroxyl in the proper position for chelation with a quinone oxygen. Its alkaline salts (which have two atoms of metal in the molecule) are not easy to purify, as they are somewhat insoluble, and easily hydrolyse with separation of quinizarin. They are best recrystallised from solutions containing excess of alkali. The lithium salt is

reddish-purple, the sodium and potassium salts are deep blue-purple.

When the sodium salt was treated with salicylaldehyde it turned brown, and after standing for 24 hours and washing with ether containing salicylaldehyde, a salmon-pink solid was left. It is decomposed by organic solvents with separation of the purple salt, but it is remarkable that it can be heated under water without any sign of hydrolysis. Analysis showed that this compound is formed by the addition of four molecules of salicylaldehyde to one molecule of the disodium salt (Found: C, 64·3; H, 4·0; Na, 6·1. $C_{14}H_6O_4Na_2,4C_7H_6O_2$ requires C, 65·3; H, 3·9; Na, 6·0%): an addition compound formed from 1 mol. of a monosodium salt and one of the aldehyde would have almost the same composition (C, 65·6; H, 3·4; Na, 6·0), but that it cannot have this formula is shown by its method of preparation, and is confirmed by the composition of the lithium compound (below).

The potassium compound was made in the same way, and had very similar properties (Found: K, 9·7. $C_{14}H_6O_4K_2,4C_7H_6O_2$ requires K, 9·7%).

These are the first recognised 6-covalent compounds of the alkali metals. If their formulation is correct, lithium cannot form an analogous compound, since its covalency is limited to 4; the salt can therefore only take up one molecule of the aldehyde for each lithium atom. The lithium compound was made in the same way as those of sodium and potassium, and has very similar properties. Analysis showed that it has the expected composition (Found: Li, 2·7. $C_{14}H_6O_4Li_2,2C_7H_6O_2$ requires Li, 2·8%).

We are indebted to Messrs. Brunner Mond and Co. for a grant from which part of the expenses of this research were met.

Dyson Perrins Laboratory, Oxford. [*Received, August 7th*, 1925.]

CCCXXV.—*Studies in the Configuration of αα′-Dibromodibasic Acids. Part IV. The αα′-Dibromoglutaric Acids.*

By Harry Raymond Ing and William Henry Perkin, jun.

The previous sections of this research dealt with the determination of the configurations of the αα′-dibromoadipic acids (J., 1921, **119**, 1393; 1924, **125**, 1492) and of the αα′-dibromosuccinic acids (J., 1924, **125**, 1814). The present communication contains the results of similar investigations with the αα′-dibromoglutaric acids.

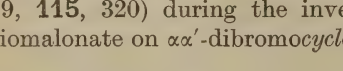
The dibromination of glutaric acid yields a mixture of two isomeric αα′-dibromoglutaric acids, one of which melts at 170° and

the other at 142° (Ingold, J., 1921, **119**, 312). The same two acids had previously been obtained by Thiele (*Annalen*, 1901, **314**, 305) by the oxidation of the *cis*- and *trans*-forms of 1 : 4-dibromo-2 : 3-dihydroxy*cyclo*pentane, the *cis*-form yielding the high-melting and the *trans*-form the low-melting acid; from this result Thiele concluded that the acid, m. p. 170°, was the *meso*-isomeride and the acid, m. p. 142°, the racemic acid. Ingold (*loc. cit.*) has brought forward evidence, based on the conversion of the dibromoglutaric acids into the corresponding dihydroxyglutaric acids, which supports Thiele's conclusions.

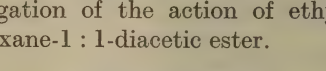
The ethyl esters of the αα′-dibromoglutaric acids are obtained as a liquid mixture of the *meso*- and *dl*-isomerides when the dibrominated glutaryl chloride is poured into ethyl alcohol, and this mixture cannot be separated into its components with certainty. One of the methyl esters, however, *viz.*, that of the dibromoglutaric acid, m. p. 170°, melts at 45°, whereas that of the acid, m. p. 142°, is a liquid, so that these esters can be obtained separate.

The dibromoglutaric esters were converted by heating with sodium iodide in alcohol into the corresponding di-iodo-esters. *Methyl di-iodoglutarate* was found to exist in a solid form, m. p. 75°, and a liquid form.

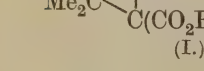
It was thought possible that the condensation of ethyl αα′-dibromoglutarate with 2 mols. of ethyl sodiomalonate might proceed in either or both of two ways, leading to a *cyclo*butane or to a *cyclo*propane ester. Thus trimethylene dibromide with ethyl sodiomalonate yields *cyclo*butanedicarboxylic ester, but the ββ-disubstituted αα′-dibromoglutaric esters which have been investigated yield only *cyclo*propane derivatives. αα′-Dibromo-ββ-dimethylglutaric ester, $CO_2Et{\cdot}CHBr{\cdot}CMe_2{\cdot}CHBr{\cdot}CO_2Et$, was found by Perkin and Thorpe (J., 1901, **79**, 729) to yield not the expected *cyclo*butane ester, but only the *cyclo*propanemalonic ester (I), which by the further action of sodium ethoxide gave rise to the yellow sodium derivative (II) of ethyl ketodimethyl*bicyclo*pentanetricarboxylate. Similar results were obtained by Ingold and Thorpe (J., 1919, **115**, 320) during the investigation of the action of ethyl sodiomalonate on αα′-dibromo*cyclo*hexane-1 : 1-diacetic ester.



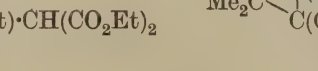
(I.)



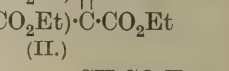
(II.)



(III.)



(IV.)



(V.)

The product of the condensation of αα′-dibromoglutaric ester with sodiomalonic ester might be either *cyclo*propane-1 : 2-dicarboxylic-1-malonic ester (IV), derived from the intermediate 1-bromo*cyclo*propane-1 : 2-dicarboxylic ester (III), or *cyclo*butane-1 : 2 : 2 : 3-tetracarboxylic ester (V). Actually both types of ring formation take place. The product of the condensation of ethyl dibromoglutarate * with ethyl sodiomalonate in alcoholic solution consisted of unchanged ethyl malonate, ethyl bromo*cyclo*propanedicarboxylate (III), and an oil of the composition $C_{16}H_{24}O_8$. The bromo*cyclo*propane ester was identified by hydrolysis to 1-bromo*cyclo*propane-1 : 2-dicarboxylic acid, m. p. 175°, first described by Ingold (*loc. cit.*, p. 314). The oil $C_{16}H_{24}O_8$ was shown to be *ethyl* cyclo*butanetetracarboxylate* (V) by the following facts : it did not yield a methyl derivative when digested with sodium ethoxide and methyl iodide and therefore did not contain a hydrogen atom replaceable by sodium ; and on hydrolysis with hydrochloric acid it was converted into a mixture of the *cis*- and *trans*-forms of *cyclo*butane-1 : 2 : 3-tricarboxylic acid, first obtained by Goldsworthy and Perkin (J., 1914, **105**, 2665). The yield of ethyl *cyclo*butanetetracarboxylate was not more than 40—50% of the theoretical and the bromo*cyclo*propane ester represented only a small fraction of the original dibromo-ester. The red aqueous solution left after extraction of the oily product of the reaction contained the remainder of the product and on acidification it deposited a thick, red oil which could not be distilled owing to decomposition, but which on analysis gave figures corresponding to $C_{14}H_{18}O_7$, which formula differs from that of the *cyclo*butane ester, $C_{16}H_{24}O_8$, by C_2H_6O. It is difficult to see how the *cyclo*butane ester (V) could lose alcohol under the conditions of the experiment, but the *cyclo*propanemalonic ester (IV) might do so with the formation of the bridged-ring ester (VI), and although the ester of formula (IV) was not actually isolated, it seems probable that it would result from the action of sodiomalonic ester on the bromo*cyclo*propane ester (III) and that it would easily lose alcohol under the conditions of the experiment with the formation of the ester (VI) and thus escape isolation.

In order to test this view, ethyl bromo*cyclo*propanedicarboxylate (III) was condensed with ethyl sodiomalonate. No *cyclo*propanemalonic ester (IV) was isolated, but the aqueous extract of the reaction product yielded on acidification a thick, red oil which, after purification by solution in alkali and reprecipitation, had the composition $C_{14}H_{18}O_7$ and was evidently identical with the substance described above.

* Unless otherwise stated, the ethyl and methyl dibromoglutarates used in these condensations were mixtures of the *meso*- and *dl*-isomerides.

This experiment was repeated, using *methyl* 1-*bromo*cyclo*propane*-1 : 2-*dicarboxylate* and methyl sodiomalonate, a pale yellow, crystalline *sodium* derivative (VII) being obtained. This substance is

(VI.) $CH_2<\begin{matrix}C(CO_2Et)\cdot CO\\ C(CO_2Et)\cdot CH\cdot CO_2Et\end{matrix}$ $CH_2<\begin{matrix}C(CO_2Me)\cdot C\cdot ONa\\ C(CO_2Me)\cdot C\cdot CO_2Me\end{matrix}$ (VII.)

(VIII.) $CH_2<\begin{matrix}C(CO_2Me)\cdot CO\\ C(CO_2Me)\cdot CH\cdot CO_2Me\end{matrix}$

fairly soluble in water, the neutral solution giving a red colour with ferric chloride. When the aqueous solution is acidified, a solid is precipitated which after recrystallisation melts at 200°, has the composition $C_{11}H_{12}O_7$, and in our view is most probably methyl keto*bicyclo*pentanetricarboxylate (VIII).

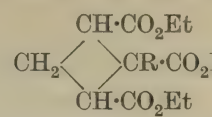
If this view is correct, this substance has a special importance, because it is the parent substance of ethyl ketodimethyl*bicyclo*-pentanetricarboxylate discovered by Perkin and Thorpe (*loc. cit.*), which has been the subject of so much important investigation at the hands of Professors Thorpe and Ingold and their collaborators. The substance described by us is being submitted to a detailed examination in Professor Ingold's laboratory.

It is evident, therefore, that in the condensation of dibromoglutaric ester with sodiomalonic ester two reactions take place simultaneously, the one leading to a *cyclo*butane and the other to a *cyclo*propane ester. In alcoholic solution these two reactions proceed to about equal extents, but in the absence of alcohol, *e.g.*, in benzene solution, the *cyclo*butane ring formation predominates, the yield of *cyclo*butane ester rising to 70—80% of the theoretical.

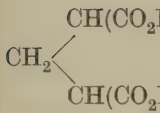
Ethyl dibromoglutarate was also condensed with the sodium derivatives of cyanoacetic, benzoylacetic, and acetoacetic esters. With ethyl sodiocyanoacetate in alcoholic solution, a 70% yield of *ethyl* 2-*cyano*cyclo*butane*-1 : 2 : 3-*tricarboxylate* (IX) was obtained, together with a small amount of ethyl bromo*cyclo*propanedicarboxylate. There was no evidence of the formation of a bridged-ring ester. The cyano*cyclo*butane ester (IX) on hydrolysis gave a mixture of the *cis*- and *trans*-modifications of *cyclo*butane-1 : 2 : 3-tricarboxylic acid.

The condensation of dibromoglutaric ester with ethyl sodiobenzoylacetate might give rise either to a benzoyl*cyclo*butane ester (X) or to a six-membered heterocyclic ester (XI). Actually *ethyl* 2-*benzoyl*cyclo*butane*-1 : 2 : 3-*tricarboxylate* (X) is formed to the extent of 30% of the theoretical, as was shown by its hydrolysis to benzoic acid and *cyclo*butanetricarboxylic acid. The other

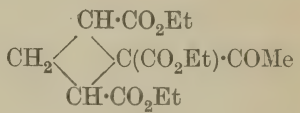
products of the reaction were unchanged ethyl benzoylacetate and ethyl bromo*cyclo*propanedicarboxylate (III).



(IX, R=CN; X, R=COPh.)

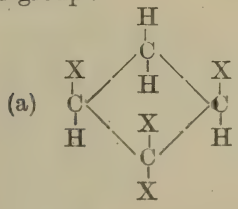


(XI.)

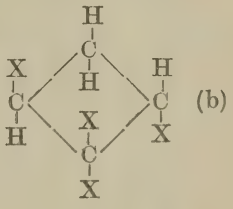
(XII.) 

Similar results were obtained in an investigation of the action of dibromoglutaric ester on ethyl sodioacetoacetate, *ethyl* 2-*aceto*-cyclo*butane*-1 : 2 : 3-*tricarboxylate* (XII) being formed in about 30% yield. Attempts to hydrolyse the benzoyl- and acetyl-*cyclo*butane esters so as to obtain the corresponding acyl-*cyclo*butane acids were not successful, the acyl groups being removed by alcoholic potash even in the cold.

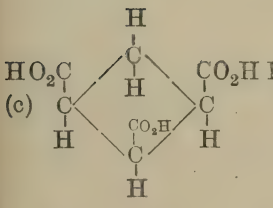
The ethyl dibromoglutarate used in all the condensations described above was a mixture of the *meso*- and *dl*-isomerides and consequently it was important to discover whether ethyl *cyclo*-butanetetracarboxylate formed from it was also a mixture. That this ester can exist as two stereoisomerides will be obvious from a consideration of the figures set out below, where X represents the ester group :



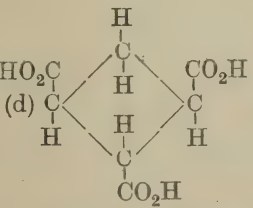
(a)



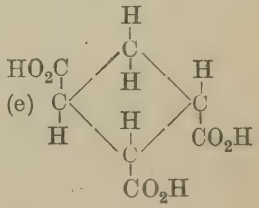
(b)



(c)



(d)



(e)

(a) represents a non-resolvable *meso*-form which would on hydrolysis and loss of carbon dioxide yield either or both of the two possible *meso*-forms of *cyclo*butane-1 : 2 : 3-tricarboxylic acid (c and d). (b) represents a racemic form which on hydrolysis and loss of carbon dioxide could give rise only to the racemic form (e)

of *cyclo*butanetricarboxylic acid. That the *cyclo*butane ester obtained in these condensations was actually a mixture of the two possible forms was made probable by the fact that two *cyclo*butanetricarboxylic acids were obtained by its hydrolysis, and it was confirmed by employing methyl dibromoglutarate with methyl sodiomalonate; two forms of *methyl* cyclo*butanetetracarboxylate* were then obtained, one a solid, m. p. 78°, and the other a liquid, b. p. 193—195°/15 mm. In the same way with methyl sodiocyanoacetate, two forms of *methyl cyano*cyclo*butanetricarboxylate* were obtained, one a solid, m. p. 111—112°, and the other a liquid, b. p. 195°/11 mm.

The *meso-* and *dl*-isomerides of methyl dibromoglutarate can be obtained separately in the pure state, since one of them is a solid (see p. 2393), so that it was important to discover whether each of the pure isomerides gave only one *cyclo*butane ester or a mixture of the two possible forms. The pure solid and liquid forms of methyl dibromoglutarate were separately condensed in benzene solution with methyl sodiomalonate and in each case a mixture of the two modifications of methyl *cyclo*butanetetracarboxylate was obtained. Similarly with methyl sodiocyanoacetate in alcoholic solution, a mixture of the two forms of methyl cyano*cyclo*butanetricarboxylate was obtained from both the solid and the liquid form of methyl dibromoglutarate. Consequently no conclusion can be drawn from these condensations as to the configuration of the dibromoglutaric acids corresponding to these esters.

Moreover it was found that the liquid methyl dibromoglutarate was readily transformed into the solid isomeride by sodium methoxide in methyl-alcoholic solution. This transformation is analogous to that which occurs with the $\alpha\alpha'$-dibromo- and $\alpha\alpha'$-di-iodo-adipic esters (compare Part II, J., 1924, **125**, 1945). The transformation did not appear to be quantitative, but as methyl dibromoglutarate reacts very readily with sodium methoxide with loss of hydrogen bromide even at low temperatures, it was difficult to be certain on this point. The liquid modification of methyl di-iodoglutarate was also largely transformed by sodium methoxide in methyl-alcoholic solution into the solid isomeride; but part of the di-iodo-ester was converted into the iodo*cyclo*propane ester, which on hydrolysis gave 1-*iodo*cyclo*propane*-1 : 2-*dicarboxylic acid*, m. p. 175—176°.

Of the two forms of methyl *cyclo*butanetetracarboxylate, it is probable that the liquid form corresponds to the *meso*-configuration (a) and the solid to the racemic configuration (b) (p. 2391). The two esters were separately hydrolysed under identical conditions. The *cyclo*butanetricarboxylic acid obtained from the solid ester

melted at 171—172° and is therefore identical with the acid termed *trans* by Goldsworthy and Perkin (*loc. cit.*). The acid obtained from the liquid ester melted at 144—145° and is consequently identical with the acid named *cis* by these authors. It seems probable that the high-melting acid has the *trans* or racemic configuration (e) and that the low-melting acid has one of the *cis*- or *meso*-configurations (c and d).

An attempt was made to settle the configuration of the acid, m. p. 171—172°, by resolution into optical enantiomorphs, but unexpected difficulty was encountered. After six recrystallisations of the brucine salt of this acid, only a very slightly dextrorotatory acid was obtained. A second attempt with quinine as the active base was more successful, an acid of $[\alpha]_D^{18°}$ 31·34° being obtained, but the pure *d-cyclo*butanetricarboxylic acid has not yet been isolated. Sufficient evidence, however, has been obtained to indicate that the high-melting acid has the *dl*-configuration (e). It is hoped to investigate further the configurations of the *cyclo*butanetricarboxylic acids.

Experimental.

The αα′-Dibromoglutaric Esters.—The methyl and ethyl esters of the αα′-dibromoglutaric acids were prepared from glutaric acid by Ingold's method (J., 1921, **119**, 316), mixtures of the *meso*- and *dl*-isomerides being obtained. Ethyl αα′-dibromoglutarate distilled at 162°/14 mm. (Found: Br, 46·4. Calc., Br, 46·2%), and the methyl ester at 150°/14 mm. (Found: Br, 50·2. Calc., Br, 50·3%).

The methyl ester of the *meso*-dibromoglutaric acid, m. p. 170°, was obtained by boiling the pure acid in methyl alcohol containing 10% of its weight of sulphuric acid. After being distilled under reduced pressure, this ester solidified and was recrystallised from methyl alcohol. *Methyl* meso-*αα′-dibromoglutarate* so obtained melts at 45° (Found: Br, 50·5. $C_7H_{10}O_4Br_2$ requires Br, 50·3%).

The methyl ester of the *dl*-dibromoglutaric acid, m. p. 142°, obtained in a similar manner was an oil, b. p. 143—145°/10 mm.

The αα′-Di-iodoglutaric Esters.—Methyl dibromoglutarate was heated in methyl-alcoholic solution with sodium iodide, and the product poured into ice-water. The semi-solid mass so obtained was filtered and the solid recrystallised three times from methyl alcohol. *Methyl αα′-di-iodoglutarate* crystallises in prisms, m. p. 75° (Found: I, 61·8. $C_7H_{10}O_4I_2$ requires I, 61·6%).

The oil left after filtering off the solid ester was extracted with ether, the ether solution washed with sodium thiosulphate solution to remove free iodine, then with water and finally dried with sodium sulphate. After evaporation of the ether a pale yellow oil was

left which showed no sign of crystallisation at — 20° (Found: I, 61·9%). This liquid *methyl di-iodoglutarate* gradually turns brown owing to the liberation of free iodine and is slowly transformed into the stable solid isomeride. It cannot be distilled without extensive decomposition.

Action of Sodium Methoxide on the Dibromo- and Di-iodo-glutaric Esters.—Liquid methyl dibromoglutarate (7 g.), dissolved in methyl alcohol (10 c.c.), was treated with a solution of sodium (0·25 g.) in methyl alcohol (10 c.c.); after 10 minutes, 5 g. of the solid ester had crystallised. With a larger proportion of sodium methoxide, sodium bromide is precipitated and methyl bromo*cyclo*propane-dicarboxylate formed.

Liquid methyl di-iodoglutarate was treated in a similar manner. A small proportion of the solid isomeride crystallised, but the di-iodo-ester reacted readily with sodium methoxide with the formation of an iodo*cyclo*propane ester and sodium iodide even at — 20°.

At the ordinary temperature methyl di-iodoglutarate is rapidly converted by sodium methoxide into methyl iodo*cyclo*propane-dicarboxylate, which on hydrolysis with hydrochloric acid yields 1-*iodo*cyclo*propane*-1 : 2-*dicarboxylic acid*. This acid is readily soluble in water but can be recrystallised from hydrochloric acid; it melts at 176—177° (Found: C, 23·6; H, 1·9; I, 49·8. $C_5H_5O_4I$ requires C, 23·4; H, 1·9; I, 49·6%).

Condensation of the αα′-Dibromoglutaric Esters with Sodiomalonic Ester.—Sodium (5 g.) was dissolved in alcohol (80 c.c.), treated with ethyl malonate (36 g.), the whole cooled in ice, and ethyl dibromoglutarate (38 g.) added slowly. After standing for an hour, the mixture was boiled on the steam-bath for an hour. The product was poured into water, the oil extracted with ether and, after evaporation of the ether, fractionated under 12 mm. The following fractions were obtained: (1) below 110°; (2) 110—170°; (3) 190—200°. Fraction (1) consisted of unchanged ethyl malonate; fraction (2) was hydrolysed with hydrochloric acid, and the acid obtained recrystallised from acetone–benzene. It was identified as 1-bromo*cyclo*propane-1 : 2-dicarboxylic acid, m. p. 175° (Ingold, *loc. cit.*) (Found: C, 28·6; H, 2·4; Br, 38·2. Calc., C, 28·7; H, 2·4; Br, 38·2%); when treated with aniline in ether, it gave a characteristic salt, m. p. 132°. Fraction (3) was redistilled and obtained as an oil, b. p. 195—198°/12 mm., which proved to be *ethyl* cyclo*butane*-1 : 2 : 2 : 3-*tetracarboxylate* (V) (Found: C, 56·0; H, 7·1. $C_{16}H_{24}O_8$ requires C, 55·8; H, 7·0%); the yield was about 50% of the original dibromoglutaric ester.

The aqueous solution obtained after extracting the oil with

ether was acidified, the red oil formed extracted with ether, and the ether solution washed with water and dried with calcium chloride. The oil left after evaporation of the ether could not be distilled without decomposition, but after remaining in a vacuum over sulphuric acid for some time it had the composition $C_{14}H_{15}O_7$ (Found: C, 55·7; H, 6·2. Calc., C, 56·4; H, 6·0%). It is considered to be a bridged-ring ester of constitution (VI). A thick red oil of identical composition and character was obtained by the following condensation: sodium (2·5 g.) was dissolved in alcohol (50 c.c.), treated with ethyl malonate (18 g.) and with ethyl bromo*cyclo*propanedicarboxylate (29 g.), the mixture boiled on the steam-bath for an hour and then poured into water. No *cyclo*propanemalonic ester was found, but on acidifying the aqueous solution the bridged-ring ester was precipitated.

In order to discover whether one or two *cyclo*butane esters were formed in the condensation of dibromoglutaric ester with malonic ester the condensation was repeated with the methyl esters. The reaction product was separated into unchanged methyl malonate, methyl bromo*cyclo*propanedicarboxylate, and methyl *cyclo*butanetetracarboxylate, which distilled at 193—195°/15 mm. and partly solidified in a freezing mixture. The semi-solid mass was pressed on porous plate, and the dry solid so obtained recrystallised from aqueous methyl alcohol. Solid *methyl* cyclo*butane*-1 : 2 : 2 : 3-*tetracarboxylate* crystallised in needles, m. p. 78° (Found: C, 50·0; H, 5·6. $C_{12}H_{16}O_8$ requires C, 50·0; H, 5·6%). The oil was extracted from the porous plate with ether and, after evaporation of the ether, distilled. Liquid *methyl* cyclo*butane*-1 : 2 : 2 : 3-*tetracarboxylate* distilled at 193—195°/15 mm. and showed no sign of crystallisation at − 20° (Found: C, 50·2; H, 5·5%). The total yield of methyl *cyclo*butane ester was about 30%.

This condensation was also performed in dry benzene solution. Sodium (5 g.) was finely powdered under benzene, treated with methyl malonate (29 g.), and the whole heated on the steam-bath until the sodium had disappeared. Methyl dibromoglutarate (34 g.) was added, and the mixture boiled for 2 hours. The product was washed with water, the benzene distilled off, and the residual oil fractionated, a 70—80% yield of *cyclo*butane ester being thus obtained.

The pure *meso*- and *dl*-isomerides of methyl dibromoglutarate were separately condensed in benzene solution with methyl malonate and in both cases a mixture of the solid and liquid forms of methyl *cyclo*butanetetracarboxylate was obtained.

Synthesis of the Bridged-ring Sodium Derivative (VIII).—Methyl dibromoglutarate was treated in methyl alcohol with sodium

methoxide, the product poured into water, the oil extracted with ether, and the crude ester fractionated, *methyl* 1-*bromo*cyclo*propane*-1 : 2-*dicarboxylate* distilling at 134—135°/15 mm. (Found: Br, 33·5. $C_7H_9O_4Br$ requires Br, 33·7%).

Sodium (6·5 g.) was dissolved in methyl alcohol (80 c.c.), mixed with methyl malonate (19 g.) and methyl bromo*cyclo*propanedicarboxylate (33 g.), and the whole boiled on the steam-bath for 6 hours. The yellow solid formed was filtered off, stirred with a little water to remove sodium bromide, and again filtered. The *sodium* derivative was recrystallised from methyl alcohol, in which it was sparingly soluble (Found: Na, 8·0. $C_{11}H_{11}O_7Na$ requires Na, 8·3%).

The aqueous solution of the sodium derivative was acidified, and the precipitated solid purified by solution in ammonia and reprecipitation. It was recrystallised from chloroform–carbon tetrachloride and finally from aqueous methyl alcohol. The substance melted at 200° and is provisionally represented by formula (VIII) (Found: C, 51·5; H, 5·0. $C_{11}H_{12}O_7$ requires C, 51·5; H, 4·7%).

Condensation of the αα′-Dibromoglutaric Esters with Sodiocyanoacetic Ester.—Sodium (5 g.) was dissolved in alcohol, treated with ethyl cyanoacetate (25 g.), and to the cold mixture ethyl dibromoglutarate (38 g.) was added. The mixture was boiled on the steam-bath for 2 hours, poured into water, and the oil extracted with ether. No oil was formed on acidifying the aqueous solution. After evaporation of the ether, the residual oil was distilled under 20 mm. and the following fractions were obtained: (1) below 120°, mainly ethyl cyanoacetate; (2) 120—190°, a few drops only; (3) 190—220°. Fraction (3) was redistilled and 23 g. of *ethyl* 2-*cyano*cyclo*butane*-1 : 2 : 3-*tricarboxylate* (IX), b. p. 210—215°/20 mm., were obtained (Found: N, 4·3. $C_{14}H_{19}O_6N$ requires N, 4·7%).

The cyano-ester was hydrolysed by cold alcoholic potash to the *tripotassium* salt of an amide-acid (Found: K, 34·5. $C_8H_6O_7NK_3$ requires K, 34·0%). Hydrolysis with hydrochloric acid yielded *cyclo*butanetricarboxylic acid.

The pure solid and liquid forms of methyl dibromoglutarate were separately condensed with methyl sodiocyanoacetate, and in both cases a mixture of a solid and a liquid form of methyl cyano*cyclo*butanetricarboxylate was obtained, the total yield being about 60% of the theoretical. Solid *methyl* 2-*cyano*cyclo*butane*-1 : 2 : 3-*tricarboxylate* crystallises from ether in prisms, m. p. 111—112° (Found: N, 5·5. $C_{11}H_{13}O_6N$ requires N, 5·5%). The liquid isomeride distils at 185—190°/12 mm. (Found: N, 5·8%). The proportion

of solid to liquid isomeride formed from the solid methyl dibromoglutarate was 1 : 2, and from the liquid dibromo-ester 1 : 3.

Condensation of Ethyl αα′-Dibromoglutarate with Ethyl Sodiobenzoylacetate.—Sodium (5 g.) was dissolved in alcohol, treated with ethyl benzoylacetate (41 g.), the mixture cooled in ice, and ethyl dibromoglutarate (37 g.) added. The reaction mixture was boiled on the steam-bath for 6 hours, the product poured into water, the oil extracted with ether and, after evaporation of the ether, fractionated. The following fractions were obtained: (1) below 150°, 10 g.; this consisted almost entirely of ethyl bromo*cyclo*propanedicarboxylate (yield about 40% of the dibromo-ester used). (2) 150—220°; this consisted of unchanged ethyl benzoylacetate. (3) 230—240°, 12 g.; this proved to be *ethyl* 2-*benzoyl*cyclo*butane*-1 : 2 : 3-*tricarboxylate* (Found: C, 64·4; H, 6·4. $C_{20}H_{24}O_7$ requires C, 63·8; H, 6·4%); yield about 30% of the original dibromo-ester.

The ester was hydrolysed by boiling with alcoholic potash. Water was added, the alcohol evaporated, the solution acidified, and the oily solid so formed extracted with ether, which removed benzoic acid (m. p. 121°). The aqueous solution was evaporated to dryness with hydrochloric acid, and the residue extracted with ether in a Soxhlet apparatus. The ether was evaporated, the residual syrup taken up with water, the solution filtered and left in a vacuum over sulphuric acid; *cis-cyclo*butanetricarboxylic acid, m. p. 143°, slowly crystallised.

Condensation of Ethyl αα′-Dibromoglutarate with Ethyl Sodioacetoacetate.—This condensation was performed in an exactly similar manner to that described above. The main products of the reaction were ethyl bromo*cyclo*propanedicarboxylate (40% of theoretical) and *ethyl* 2-*acetyl*cyclo*butane*-1 : 2 : 3-*tricarboxylate* (30% of theoretical), b. p. 195°/18 mm. (Found: C, 56·8; H, 7·1. $C_{15}H_{22}O_7$ requires C, 57·3; H, 7·0%). The ester was hydrolysed in the usual way with alcoholic potash and *cis-cyclo*butanetricarboxylic acid, m. p. 143°, was obtained.

The cyclo*Butane*-1 : 2 : 3-*tricarboxylic Acids.*—When ethyl *cyclo*butanetetracarboxylate was hydrolysed by boiling with hydrochloric acid, a mixture of two *cyclo*butanetricarboxylic acids was obtained, which was difficult to separate into its components. The mixture, which began to melt at 135° but was not completely molten until 160°, contained *cis-cyclo*butane-1 : 2 : 3-tricarboxylic acid, m. p. 143°, and *trans-cyclo*butane-1 : 2 : 3-tricarboxylic acid, m. p. 172° (Goldsworthy and Perkin, J., 1914, **105**, 2665).

The solid and liquid forms of methyl *cyclo*butanetetracarboxylate were separately hydrolysed in an identical manner. Each ester

was kept with methyl-alcoholic potash for several days, water was then added, and the alcohol evaporated. The solution was neutralised with dilute nitric acid, and the lead salt precipitated with lead nitrate. The lead salt suspended in water was decomposed with hydrogen sulphide, and the filtered solution evaporated. In each case a clear syrup was obtained which showed no sign of crystallisation. It was heated at 150° until no more carbon dioxide was evolved; the residue was dissolved in hot water and left in a desiccator to crystallise. The acid obtained from the solid ester solidified completely and was recrystallised from hydrochloric acid; it melted at 171—172° and was therefore *trans-cyclo*butane-1 : 2 : 3-tricarboxylic acid (Found: C, 44·5; H, 4·3. Calc., C, 44·7; H, 4·2%).

The acid obtained from the liquid *cyclo*butane ester deposited first a small amount of the *trans*-acid, but the residual syrup eventually solidified and after recrystallisation from hydrochloric acid melted at 144—145°. It was therefore *cis-cyclo*butane-1 : 2 : 3-tricarboxylic acid (Found: C, 44·5; H, 4·1%).

Resolution of trans-cyclo*Butane*-1 : 2 : 3-*tricarboxylic Acid*.—The tricarboxylic acid (15 g.) was dissolved in hot water (360 c.c.), mixed with brucine (113 g.), the whole heated on the steam-bath, the excess of brucine filtered off, and the filtrate allowed to cool. The brucine salt which separated was recrystallised a number of times from water; the rotation was observed each time in a 2-dcm. tube, the amount of substance taken being made up to 20 c.c. with methyl alcohol.

	1	2	3	4	5	6
G. of salt	0·2406	0·1120	0·1308	0·1150	0·1034	0·1232
α obs.	−1·16°	−0·41°	−0·47°	−0·41°	−0·37°	−0·44°
$[\alpha]_D^{18°}$	−38·3°	−36·6°	−35·9°	−35·6°	−35·8°	−36·1°

The rotations of the different fractions did not seem to approach a constant value. The last fraction was therefore decomposed with ammonia, and the filtrate from the precipitated brucine evaporated to dryness with a slight excess of hydrochloric acid. The residue was extracted with cold acetone; after evaporation of the acetone, a solid acid, m. p. 165—170°, was obtained which was only slightly dextrorotatory (0·1070 g. made up to 20 c.c. with water gave $\alpha = +0·04°$ in a 2-dcm. tube at 18°; whence $[\alpha]_D^{18°} = +3·7°$).

In a second attempt, the acid (1 mol.) was mixed with quinine (2 mols.) dissolved in alcohol; after standing for an hour, the salt which had separated was collected and decomposed with ammonia. The acid so obtained was then treated in a similar manner. The salt formed had the composition $C_7H_8O_6,2C_{20}H_{24}O_2N_2,C_2H_6O$

(Found: C, 66·9; H, 6·9; N, 6·3. $C_{49}H_{62}O_{10}N_4$ requires C, 66·7; H, 7·0; N, 6·3%). After three operations, an acid was obtained, m. p. 155—160°, of which 0·1340 g. made up to 20 c.c. with water gave $\alpha = +0{\cdot}42°$; whence $[\alpha]_D^{18°} = +31{\cdot}34°$. Owing to the small amount of acid available, it was not possible to proceed further with the resolution, but sufficient evidence has been obtained that the *trans-cyclo*butanetricarboxylic acid, m. p. 172°, has the *dl*-configuration.

One of us (H. R. I.) wishes gratefully to acknowledge the receipt of a grant from the Chemical Society Research Fund which has defrayed a part of the cost of this investigation.

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CCCXXVI.—*The Catalysis by Alumina of the Reaction between Ethyl Alcohol and Ammonia.*

By GORDON WILLIAM DORRELL.

PREVIOUS work on this reaction has been mainly qualitative (Sabatier and Mailhe, *Compt. rend.*, 1909, **148**, 898; 1910, **150**, 823; 1911, **153**, 160, 1204), but some quantitative results have been given by Smolenski (*Roczniki Chem.*, 1921, **1**, 232). In a paper published after the present work was finished, Brown and Reid (*J. Physical Chem.*, 1924, **28**, 1067) state that specially prepared silica gel is the most efficient catalyst for converting aliphatic alcohols into amines; they give no results for the conversion with alumina as catalyst.

The object of this research was to study the effect of varying such factors as temperature, time of contact, and the ratio of alcohol to ammonia. Throughout, the catalyst was to be the same; and alumina was finally chosen in preference to other well-known aminating catalysts, *e.g.*, thoria, because it has scarcely any dehydrogenating action upon alcohol.

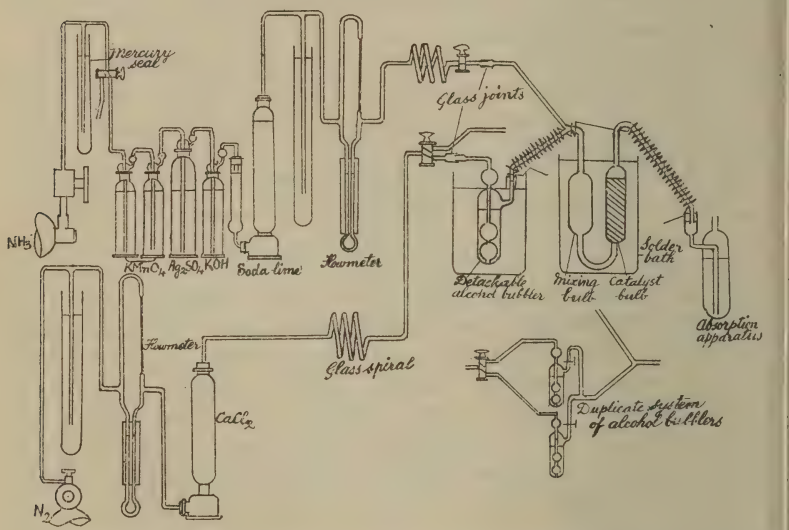
Theoretical treatment by the Nernst equation shows that the reaction: $C_2H_5{\cdot}OH + NH_3 = C_2H_5{\cdot}NH_2 + H_2O$ (where the formation of secondary and tertiary amines is ignored) is exothermic to the extent of 5920 calories, and that the amount of conversion in the system in equilibrium, although greater at low temperatures than at high, does not vary rapidly with temperature.

Apparatus and Method.—Ammonia from a cylinder (Fig. 1) was passed through two ammoniacal solutions of potassium permangan-

ate, a solution of silver sulphate, and one of caustic potash. It was then dried by soda-lime, and its rate of flow measured.

Nitrogen * from a cylinder was passed through a second flow-meter, dried by calcium chloride, and allowed to bubble through absolute ethyl alcohol (dried by potassium carbonate and distilled), immersed in a thermostat. The quantity of alcohol evaporated was determined by its temperature and by the rate of flow of the nitrogen. By electrical heating, the emerging nitrogen–alcohol mixture was kept at a temperature sufficiently high to prevent condensation of the alcohol in the connecting tubes.

FIG. 1.



The ammonia, nitrogen, and alcohol were allowed to mix and were preheated in a bulb filled with pieces of glass tube, before entering a second bulb containing the catalyst. Both bulbs were immersed in the same bath of solder, and the temperature of the catalyst was taken as that registered by a mercury thermometer (calibrated against standard thermometers) the bulb of which was situated between the preheater and the catalyst bulb.

The smaller diagram shows a modified form of the apparatus used in the later part of the work. By means of a second bubbler containing alcohol it was possible to avoid interruption in the flow of alcohol and ammonia over the catalyst while the products of the preceding experiment were being removed for analysis. In

* No difference was detected in the results of those experiments where the nitrogen had been passed over heated copper gauze.

addition, the preliminary sweeping through the apparatus with ammonia and the final washing out with nitrogen which had to be done in the first part of the work were eliminated, and a much simpler technique was evolved.

The Catalyst.—Only one sample of alumina was used, which is referred to as Al_2O_3-1. It was prepared by adding excess of ammonia, *d* 0·880, to a strong solution of aluminium nitrate, washing the precipitate, and drying it in stages at 100°, 160°, and 400°, after which it was broken into fragments about 4 mm. in diameter; these were filled into the bulb so that the catalyst, which weighed about 25 g., occupied a volume of 50 c.c.

Analysis.—The amount of alcohol used was determined by weighing the bubbler before and after the experiment. A sufficiently approximate value of the quantity of nitrogen was obtained from flowmeter–time observations. The quantity of ammonia passed (correct to 1—6%, depending upon the rate of flow of the gas) was determined directly from flowmeter–time observations; for very small gas velocities, *e.g.*, 3 c.c. per minute, this value was subject to the larger error. A more accurate value could be obtained from a knowledge of the amount of basic nitrogen absorbed in standard acid (see below); since no ammonia decomposes into nitrogen and hydrogen, and a negligible quantity of non-basic substances is produced, under the given conditions, from the decomposition of amines, the quantity of ammonia used must be equivalent to the amount of basic nitrogen absorbed in acid.

No separate analysis of each of the primary, secondary, and tertiary amines produced was made, but the three were estimated together, as "amines" or "ammonia converted," by Weber and Wilson's method (*J. Biol. Chem.*, 1918, **35**, 385), in which the solution of amines and ammonia is treated with yellow mercuric oxide, whereby ammonia is quantitatively removed. The amines were distilled from the alkaline filtrate from the mercuric oxide into standard acid, the excess of which was then estimated. The results obtained from several blank analyses with the most satisfactory mercuric oxide indicated that the probable error in the final conversion value was 0·5%.

Expression of the Results.—The percentage conversion of ammonia into amines,* $\%E$, is given by the expression Mols. of amines absorbed × 100/mols. of ammonia used. The symbol $\%E_0$ denotes the percentage conversion in the particular case where the molecular ratio of ammonia to alcohol is unity; it is calculated from the equation $\%E_0 = \%E/R$, where R = mols. of alcohol used/mols.

* No figures for the amount of conversion of alcohol into amines have been given.

of ammonia used. For example, in a series of experiments it was desired to keep the molecular ratio of alcohol to ammonia equal to 1·0; but experimentally this is difficult. Actually the ratio varied between 0·7 and 1·2. However, by dividing such a diverging molecular ratio into the corresponding $\%E$, the true value of the latter for a molecular ratio of unity is obtained. The results given later (Fig. 3) show that the correction just discussed is valid when the molecular ratio of alcohol to ammonia lies between 0·6 and 1·2.

Effect of Temperature.—The effect of varying the temperature on the amount of ammonia converted is shown in Table I.

TABLE I.

Ratio $C_2H_5{\cdot}OH : NH_3 = 1{\cdot}0$.
Mean rate of flow of NH_3 = 9·2 c.c. (at *N.T.P.*) per min.
Mean rate of flow of N_2 = 50 c.c. (at *N.T.P.*) per min.

Temp. of catalyst bath.	No. of expts.	$\%E_0$. Mean.
344°	9	11·5
293	4	15·3
239	3	9·3

Since the quantity of ammonia (or alcohol) passing over the catalyst in a given time is the same for all three temperatures, its time of contact with the catalytic surface at 344° is different from that at 239°; actually, the times of contact of 1 mol. of ammonia at 239° and 344°, respectively, are in the ratio 1·2 : 1. A correction for this factor, if it were possible to apply it, would not affect the values of $\%E_0$ to any serious extent.

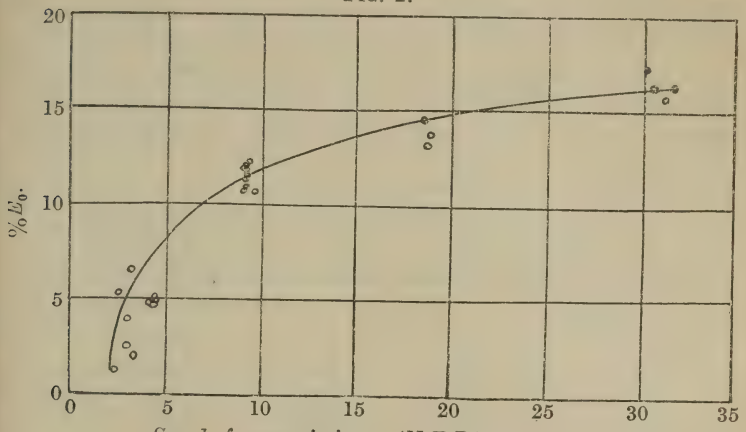
The important result of this table is that the optimum temperature of the reaction under the given conditions is about 300°.

Effect of Rate of Flow of the Reacting Gases.—The curve in Fig. 2 illustrates the results obtained in experiments at 344° in which the molecular ratio of alcohol to ammonia was 1·0 and the speed of the ammonia varied from 2 to 32 c.c. (*N.T.P.*) per minute. The rates of flow of the alcohol vapour and nitrogen were varied so that the partial pressure of the latter was always 5·6 times that of the former (or of the ammonia). The finer particles of the catalyst were carried away by the gases when the speed of the ammonia exceeded 32 c.c. per minute, and therefore the curve could not be followed experimentally up to its maximum.

Contrary to the usual experience that increased time of contact means increased amount of reaction product owing to the state of equilibrium being approached, this curve shows that the conversion of the ammonia falls off rapidly when the speed of the reacting gases diminishes, especially when the speed of the ammonia is less than 5 c.c. per minute. It will be shown later that the most probable cause of this is the decomposition of the amine itself.

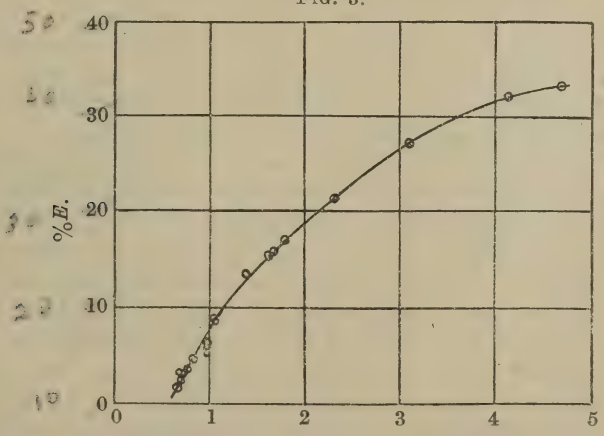
Effect of Varying Relative Quantities of Alcohol and Ammonia.—The curve in Fig. 3, plotted from the results of experiments at 344° in which the speeds of the ammonia and nitrogen were 9·4 and

FIG. 2.



50 c.c. per minute, respectively, shows the relation between $\%E$ and the molecular ratio $C_2H_5{\cdot}OH : NH_3$. It is practically linear where this ratio lies between 0·6 and 1·2; but its slope decreases

FIG. 3.



as the ratio increases, from which it is evident that the effect of using excess of alcohol is the production of larger quantities of secondary and tertiary amines, because the amount of ammonia converted per mol. of alcohol is proportionately small at large

molecular ratios, owing to one mol. of ammonia tending to react with more than one of alcohol.

The increase in activity of the catalyst indicated by the curve will be discussed later.

Decomposition of Ethylamine.—Sabatier and Gaudion (*Compt. rend.*, 1917, **165**, 222, 310), working with a nickel catalyst at 300°, were unable to decompose ethylamine into hydrogen and acetonitrile because it broke down so readily into ammonia and ethylene. Upson and Sands (*J. Amer. Chem. Soc.*, 1922, **44**, 2306) found that its decomposition, in presence of a kaolin catalyst, into ethylene and ammonia is favoured by low temperature; it can be assumed that below 500° the products are ammonia and ethylene only.

Ethylamine * was evaporated from an aqueous solution by means of a stream of nitrogen, and the mixed gases were passed over the Al_2O_3-1 catalyst at 344°. The mean speed of the nitrogen was 7 c.c. (at *N.T.P.*) per minute, and of the ethylamine 3 c.c. per minute (calc.); the duration of the experiment was 130 minutes. The products were led through standard acid, and the unabsorbed gases collected, by aspiration, over mercury. The quantities of ammonia and amines in the acid were estimated and allowance was made for the amount of ammonia present in the original ethylamine. The unabsorbed gases were analysed for ethylene. The percentage decompositions of the ethylamine calculated from the quantities of ammonia and ethylene produced were respectively 60 and 33.

These two values should be equal if ethylamine decomposes thus: $C_2H_5{\cdot}NH_2 = C_2H_4 + NH_3$. However, the smaller result alone is sufficiently large to account for the falling off in the values of $\%E_0$ when the speeds of the gases are small (Fig. 2).

Action of the Alumina Catalyst on Ammonia.—Certain irregularities were observed in the first two experiments (Nos. 1 and 2 in Table III) in connexion with the amount of ammonia passing over the catalyst; as measured by titration of the absorbing acid, there was apparently a loss of ammonia. The explanation first conceived, that some of the ammonia was being decomposed into nitrogen and hydrogen, was finally disposed of by carrying out a special gas analysis of the products obtained when ammonia and nitrogen alone were passed over the catalyst; no decomposition was detected.

The loss was finally found to be due to the adsorption of ammonia by the fresh alumina catalyst. In Table II are the results obtained with a second catalyst, which consisted of 13·5 g. of fresh alumina

* As the ethylamine contained a small quantity of ammonia, for which an approximate correction was made, the result can be regarded as qualitative only.

prepared in a similar way to Al_2O_3-1. This was kept at 344°, and nitrogen and ammonia were led over it at definite rates. The emerging gases were passed for a definite time (t) through standard acid; and the amount of ammonia present (v') was determined by back titration. The quantity of ammonia (v) entering the catalyst chamber during the same time was determined from flowmeter time observations. The amount of ammonia adsorbed by the alumina is the difference $v - v'$. The absorption acid was changed after each time interval (col. 1).

TABLE II.

Speed of NH_3 = 9—10 c.c. (at *N.T.P.*) per min. (equiv. to 246·3 c.c. of N/10-acid per hour). Speed of N_2 = 50 c.c. (at *N.T.P.*) per min.
t = time in mins. from start of flow of NH_3 over Al_2O_3. v and v' are expressed as c.c. of N/10-acid.

t.	v.	v'.	$v - v'$.
5	20·5	0·1	20·4
15	61·6	9·5	52·1
35	143·7	78·3	65·4
55	225·7	146·9	78·8
105	431·0	340·5	90·5

If a curve is drawn, the figures of column 4 being plotted against those of column 1, it will be seen that the adsorption of the ammonia is approaching its maximum value after a period of 105 minutes.

The Catalyst Al_2O_3-1.—After the preceding experiment had been made, the original catalyst was examined. Its colour had changed from white to buff; and some fragments were black throughout, showing that the reacting gases must have penetrated right into the granules.

Catalytic poisoning was entirely absent, for the mean $\%E_0$ of experiments 3—6 is 11·4 and of experiments 19—23, 11·6 (Table III).

The increase in activity of the catalyst referred to in connexion with the curve (Fig. 3) does not affect the general results to any serious extent. Immediately before this particular series of experiments was made, the catalyst had been (1) accidentally shaken, (2) thoroughly saturated with ethylamine vapour during the work on the decomposition of this substance. It is quite possible that its activity would change as a result of such treatment. Pease and Yung (*J. Amer. Chem. Soc.*, 1924, **46**, 390) found that alumina which had been used in the catalytic decomposition of ether appeared to be activated with respect to alcohol, and the yield of ethylene was nearly doubled.

Experimental Results in Detail.—In Table III are the more important data appertaining to the experiments; these were carried out in the order given.

TABLE III.

No. of expt.	Temp. of catalyst.	Speed of NH_3 in c.c./min. (*N.T.P.*).	Speed of N_2 in c.c./min. (*N.T.P.*).	Duration of expt. in mins.	Ratio of alcohol to ammonia.	% *E*.	% E_0.
1	344°	5·0	50	31·5	1·60	2	—
2	,,	8·5	,,	32	0·89	5·8	—
3	,,	9·4	,,	60	0·76	9·4	12·3
4	,,	9·1	,,	40	1·06	11·3	10·7
5	,,	9·6	,,	50	0·91	9·7	10·7
6	,,	9·2	,,	70	0·94	11·4	12·1
7	293	9·0	50	45	0·99	15·3	15·5
8	,,	9·4	,,	50	0·95	16·3	17·1
9	,,	8·8	,,	40	1·14	14·4	12·6
10	,,	9·0	,,	,,	1·06	16·6	15·7
11	239	5·7	50	40	1·33	12·4	9·3
12	,,	9·0	,,	50	0·94	8·4	9·0
13	,,	9·2	,,	60	0·95	9·0	9·5
14	344	3·3	17	60	0·57	1·2	2·1
15	,,	2·4	,,	45	0·58	3·1	5·3
16	,,	2·3	20	60	0·97	1·2	1·3
17	,,	2·9	,,	,,	0·65	1·7	2·6
18	,,	3·0	,,	70	0·70	2·8	4·0
19	,,	9·2	50	40	0·92	9·9	10·8
20	,,	9·1	,,	,,	0·87	9·9	11·3
21	,,	9·2	,,	,,	0·87	10·1	11·7
22	,,	9·2	,,	,,	0·85	10·3	12·1
23	,,	9·2	,,	,,	1·13	13·4	11·9
24	344	18·7	100	30	0·93	12·3	13·2
25	,,	18·8	,,	,,	0·93	12·6	13·6
26	,,	18·6	,,	,,	0·93	13·5	14·5
27	344	4·2	25	40	0·74	3·6	4·9
28	,,	4·4	,,	60	0·73	3·7	5·1
29	,,	4·5	,,	,,	0·70	3·4	4·9
30	,,	4·5	,,	,,	0·75	3·7	4·9
31	344	3·0	20	330	0·87	5·8	6·7
32	344	30·7	160	30	0·87	14·2	16·3
33	,,	31·7	,,	,,	0·90	14·7	16·3
34	,,	31·2	,,	,,	0·94	14·7	15·6
35	,,	30·2	,,	,,	1·00	17·6	17·6
36	345	9·7	48	50	1·61	25·6	
37	344	9·8	,,	60	1·38	23·5	
38	,,	10·0	50	50	0·97	16·2	
39	,,	9·3	,,	45	1·06	18·6	
40	,,	9·6	,,	,,	1·02	19·0	
41	,,	9·3	48	60	0·82	14·7	
42	343	9·4	,,	50	0·70	13·2	
43	,,	9·6	50	60	0·96	15·2	
44	,,	9·4	,,	,,	0·68	12·3	
45	344	9·1	,,	40	0·96	15·4	
46	,,	9·7	,,	,,	0·75	13·6	
47	,,	9·7	,,	30	0·67	13·2	
48	,,	9·6	,,	60	0·64	11·7	
49	343	9·3	,,	30	2·30	31·3	
50	344	9·3	,,	40	1·79	27·1	
51	,,	9·3	,,	,,	1·64	25·7	
52	,,	9·0	,,	30	3·10	37·1	
53	,,	9·2	,,	,,	4·69	43·1	
54	,,	9·0	,,	,,	4·13	42·2	

Summary.

The catalysis by alumina of the reaction between alcohol and ammonia has been studied from the point of view of the quantity of ammonia converted into amine.

The effects of varying (*a*) the temperature, (*b*) the speed of the reacting gases, (*c*) the ratio of alcohol to ammonia have been determined.

The decomposition of ethylamine itself has been found to occur under the conditions obtaining in the main reaction; ammonia is not decomposed to any measurable extent by the catalyst.

Alumina adsorbs ammonia readily, and a table is given showing the relation between the amount of ammonia adsorbed and the time of flow of the ammonia over the catalyst.

No sign of catalytic poisoning could be detected.

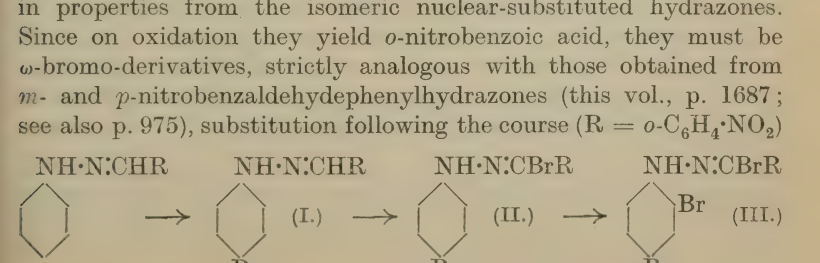
The author desires to express his thanks to Professor F. G. Donnan, who suggested the investigation; and to the Advisory Council of the Department of Scientific and Industrial Research for a maintenance grant during the period of the research.

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LONDON. [*Received, June 23rd,* 1925.]

CCCXXVII.—*Substituted* iso*Diazomethanes.*

By FREDERICK DANIEL CHATTAWAY and ARTHUR JOHN WALKER.

WHEN bromine (1 mol.) is allowed to act upon *o*-nitrobenzaldehyde-phenylhydrazone (1 mol.), the first product easily isolated is *o*-nitrobenzaldehyde-*p*-bromophenylhydrazone (I). The further action of bromine yields first an orange-red *dibromo*-derivative and finally a yellow *tribromo*-derivative, m. p. 110°. These compounds can also be formed by the bromination of the *p*-bromo- and 2 : 4-dibromophenylhydrazones of *o*-nitrobenzaldehyde, but they differ entirely in properties from the isomeric nuclear-substituted hydrazones. Since on oxidation they yield *o*-nitrobenzoic acid, they must be ω-bromo-derivatives, strictly analogous with those obtained from *m*- and *p*-nitrobenzaldehydephenylhydrazones (this vol., p. 1687; see also p. 975), substitution following the course (R = *o*-C_6H_4·NO_2)



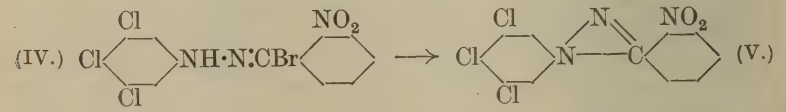
The final product, *ω-bromo-o-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone* (III), can be recrystallised without change from chloroform, benzene, or acetic acid, but on warming for a short time with alcohol it loses hydrogen bromide, forming a compound * which explodes with great violence when heated.

This also occurs when the ω-bromo-derivative is warmed in acetic acid with sodium acetate, but elimination of hydrogen bromide is most readily effected by shaking a solution of the ω-bromo-derivative in benzene with a little aqueous ammonia, or a small quantity of pyridine.

The action of bromine upon *o*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone yields a *trichloromonobromo*-derivative (m. p. 115°) which similarly may be made to lose hydrogen bromide and form an explosive compound containing all the original chlorine, but no bromine. The formation of the explosive compound does not therefore take place by the elimination of the nuclear, but of the ω-halogen. The occupation of both *o*-positions and the *p*-position by chlorine in this compound excludes the possibility of it being formed by the elimination of the ω-halogen with an *o*- or the *p*-hydrogen of the phenylhydrazine nucleus.

In a similar way, the formation of an explosive derivative from *ω-bromo-o-nitrobenzaldehyde-3 : 4 : 5-trichlorophenylhydrazone* (IV), in which both the *m*-positions are occupied, excludes the possibility of an elimination of hydrogen bromide between the ω-bromine and the hydrogen in the *m*-position.

The most probable explanation of the reaction is that the ω-halogen is eliminated with the imino-hydrogen of the hydrazone, forming an unstable, three-atom *iso*diazomethane ring, thus :



If the bromination of *o*-nitrobenzaldehydephenylhydrazone be carried out in the presence of sodium acetate, the formation of ω-bromo-*o*-nitrobenzaldehyde-*p*-bromophenylhydrazone and the elimination of hydrogen bromide from this take place successively, yielding the explosive 1-p-*bromophenyl*-3-o-*nitrophenyl*isodiazomethane (VI) as the product of the one operation :

* Ciusa and Vecchiotti (*Gazzetta*, 1916, **46**, i, 240) appear to have had this compound in their hands, but as they failed to observe the loss of hydrogen bromide during recrystallisation from alcohol, they assumed that it was an ω-bromo-derivative, having a structure which we have shown to be that of the entirely different compound, m. p. 110°.

$$C_6H_5\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot NO_2 \longrightarrow C_6H_4Br\cdot NH\cdot N{:}CBr\cdot C_6H_4\cdot NO_2 \longrightarrow$$
$$C_6H_4Br\cdot N\overset{N}{\diagup\!\!\diagdown}C\cdot C_6H_4\cdot NO_2 \quad \text{(VI.)}$$

An excess of bromine has no action on this final explosive product under the conditions of the experiment, as might be expected, there being no hydrogen attached to the nitrogen united with the aryl residue, replacement of which by halogen appears to be a necessary preliminary to the intramolecular rearrangement by which it passes into the nucleus.

Other ω-bromo-*o*-nitrobenzaldehydehydrazones yield similar explosive compounds, which also must therefore be regarded as *iso*diazomethanes, *e.g.*,

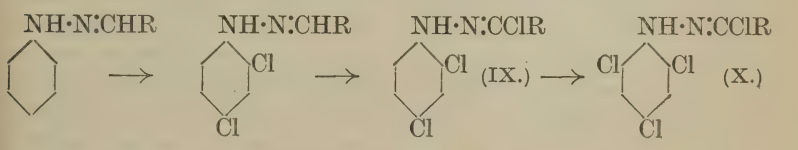
(VII.) $(2:4\text{-})C_6H_3Br_2\cdot N\overset{N}{\diagup\!\!\diagdown}C\cdot C_6H_4\cdot NO_2$ and

$(2:4:6\text{-})C_6H_2Cl_3\cdot N\overset{N}{\diagup\!\!\diagdown}C\cdot C_6H_4\cdot NO_2$ (VIII.)

The action of chlorine upon *o*-nitrobenzaldehydephenylhydrazone is similar to the action of bromine, although naturally more energetic. The first product easily isolated is *o*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone. The further action of chlorine upon this yields a trichloro-derivative (m. p. 132°) which must be *ω-chloro-o-nitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone*,

$$C_6H_3Cl_2\cdot NH\cdot N{:}CCl\cdot C_6H_4\cdot NO_2 \text{ (IX)},$$

since it differs in its properties from *o*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone and yields *o*-nitrobenzoic acid on oxidation. The final product of the chlorination is a tetrachloro-derivative, which, since it can also be obtained by the chlorination of *o*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone, must be *ω-chloro-o-nitrobenzaldehyde*-2 : 4 : 6-*trichlorophenylhydrazone* (X). The course of the reaction may therefore be represented thus (R = o-$C_6H_4\cdot NO_2$) :



Like the ω-bromo-*o*-nitrobenzaldehydephenylhydrazones, the ω-chloro-*o*-nitrobenzaldehydephenylhydrazones lose hydrogen halide when their benzene solutions are warmed with pyridine or ammonia, forming highly explosive compounds containing similar three-atom, *iso*diazomethane rings, *e.g.*, (X) ⟶ (VIII).

Experimental.

The Bromination Products of o-*Nitrobenzaldehydephenylhydrazone, and their* iso*Diazomethane Derivatives.*

To a suspension of 5 g. (1 mol.) of *o*-nitrobenzaldehydephenylhydrazone in 25 c.c. of acetic acid was added a solution of 3 g. (1 mol.) of bromine in the same solvent. An orange solution was formed, from which red crystals of *o*-nitrobenzaldehyde-*p*-bromophenylhydrazone separated, m. p. 183° after recrystallisation from alcohol.

*ω-Bromo-o-nitrobenzaldehyde-*p*-bromophenylhydrazone* (II).—The addition of more bromine (6 g.; 2 mols.) to a similar quantity of *o*-nitrobenzaldehydephenylhydrazone yielded an orange solution from which, on pouring into water, a viscid, red solid was precipitated. This was dissolved in a little warm ether and cooled, when a small quantity of red crystals of *o*-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone separated, m. p. 204° after recrystallisation from alcohol.

The ethereal mother-liquor yielded on evaporation an amorphous red solid. This lost hydrogen bromide so readily that it could not be recrystallised, but it was shown to consist of ω-bromo-*o*-nitrobenzaldehyde-*p*-bromophenylhydrazone by conversion into its crystalline *iso*diazomethane derivative (below), a yield of over 3·5 g. (90% of the theoretical) being obtained from 5 g. of the red solid.

1-p-*Bromophenyl*-3-o-*nitrophenyl*iso*diazomethane* (VI).—A solution of 5 g. of ω-bromo-*o*-nitrobenzaldehyde-*p*-bromophenylhydrazone in 20 c.c. of warm benzene was shaken with 5 c.c. of concentrated aqueous ammonia. The mixture set to a mass of yellow crystals, which were collected, and recrystallised from chloroform, in which the compound is moderately soluble, and from which it separates in yellow needles; these explode at 144° without melting * (Found: Br, 24·7; N, 12·9. $C_{13}H_8O_2N_3Br$ requires Br, 25·1; N, 13·2%).

This *iso*diazomethane is most conveniently prepared by adding to 5 g. of *o*-nitrobenzaldehydephenylhydrazone and 10 g. of anhydrous sodium acetate suspended in acetic acid, a solution of 6 g. of bromine (2 mols.) in acetic acid; the hydrazone dissolves and fine, yellow crystals of the *iso*diazomethane separate (yield 5 g. after washing with water and recrystallisation from chloroform).

* The explosion point does not vary by more than a degree with the rate of heating. It was found that the determination of a mixed explosion point (analogous with a mixed melting point) could be employed to establish the identity of these compounds, the explosion point of a mixture being generally below the explosion point of either of the pure constituents.

The same compound is obtained by the action of bromine (1 mol.) upon *o*-nitrobenzaldehyde-*p*-bromophenylhydrazone under similar conditions.

ω-Bromo-o-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone (III).—To a cooled suspension of 5 g. (1 mol.) of *o*-nitrobenzaldehydephenylhydrazone in 25 c.c. of acetic acid was added a solution of 10 g. of bromine (3 mols.) in acetic acid. A yellow solution was formed which deposited compact crystals of the ω-bromo-derivative. This crystallises from acetic acid, in which it is easily soluble, in compact, pale yellow needles, m. p. 110° (yield 7 g. or 70%). It is sparingly soluble in ligroin and easily soluble in chloroform or benzene (Found : Br, 50·4. $C_{13}H_8O_2N_2Br_3$ requires Br, 50·2%).

The same compound (m. p. 110°) was similarly prepared by adding bromine (1 mol.) to a suspension of *o*-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone in acetic acid.

A small quantity of the substance, when boiled for 3 hours with an alkaline solution of potassium permanganate, yielded *o*-nitrobenzoic acid, m. p. 144°, thus showing that no halogen had entered the aldehyde nucleus.

1-2 : 4-Dibromophenyl-3-o-nitrophenylisodiazomethane (VII).—ω-Bromo-*o*-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone (5 g.), dissolved in 25 c.c. of warm benzene, was shaken with 5 c.c. of concentrated aqueous ammonia. The mixture became hot and set to a mass of yellow crystals. These were recrystallised from chloroform, in which the compound was sparingly soluble, and from which it separated in long, yellow needles which exploded violently at 145—146° without melting (yield almost theoretical) (Found : Br, 40·5 ; *M*, ebullioscopic in chloroform, 373. $C_{13}H_7O_2N_3Br_2$ requires Br, 40·3% ; *M*, 397).

The compound can be obtained from ω-bromo-*o*-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone in several other ways. For example, it separates when dry ammonia gas is passed into a solution of the ω-bromo-derivative in benzene, or when a small quantity of pyridine is added. It is also formed when a solution of the ω-bromo-compound in acetic acid is warmed gently with sodium acetate, and when a solution of the same compound in alcohol is gently boiled for a few minutes.

ω-Bromo-o-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone, $C_6H_3Cl_2{\cdot}NH{\cdot}N{:}CBr{\cdot}C_6H_4{\cdot}NO_2$.—A solution of 2·5 g. of bromine (1 mol.) in acetic acid was added to a suspension of 5 g. of *o*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone (1 mol.) in 50 c.c. of warm acetic acid. The yellow solution formed deposited, on cooling, crystals of the *ω-bromo*-derivative in clusters of pale yellow needles, m. p. 122°. It is

moderately easily soluble in acetic acid and easily soluble in benzene (Found : Cl + Br, 38·6. $C_{13}H_8O_2N_3Cl_2Br$ requires Cl + Br, 38·8%).

1-2 : 4-*Dichlorophenyl*-3-o-*nitrophenyl*iso*diazomethane* (corresponding to VII) separated almost instantaneously when a benzene solution of ω-bromo-*o*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone was shaken with concentrated aqueous ammonia. It crystallises from chloroform, in which it is easily soluble, in bright yellow, six-sided, slender prisms which explode at 140° (Found : Cl, 23·2. $C_{13}H_7O_2N_3Cl_2$ requires Cl, 23·05%).

ω-*Bromo*-o-*nitrobenzaldehyde*-2 : 4 : 6-*trichlorophenylhydrazone*, $C_6H_2Cl_3{\cdot}NH{\cdot}N{:}CBr{\cdot}C_6H_4{\cdot}NO_2$, separated when a solution of 2·5 g. of bromine (1 mol.) was added to 5 g. of *o*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone in 50 c.c. of acetic acid. It was recrystallised from acetic acid, in which it is moderately easily soluble. It is also easily soluble in chloroform or benzene.

It exists in two polymorphic modifications, and when a solution in acetic acid is cooled separates first in light yellow needles, which in the warm solvent transform rapidly into pale yellow, compact prisms, m. p. 115—116° (Found : Cl + Br, 43·9. $C_{13}H_7O_2N_3Cl_3Br$ requires Cl + Br, 44·0%).

1-2 : 4 : 6-*Trichlorophenyl*-3-o-*nitrophenyl*iso*diazomethane* (VIII) separated when a solution of ω-bromo-*o*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone in benzene was shaken with concentrated aqueous ammonia. It dissolves easily in chloroform or benzene and sparingly in ligroin. It crystallises from chloroform–ligroin in bright yellow, long prisms, which explode at 163° (Found : Cl, 31·1; *M*, ebullioscopic in chloroform, 365. $C_{13}H_6O_2N_3Cl_3$ requires Cl, 31·1%; *M*, 343·5).

ω-*Bromo*-o-*nitrobenzaldehyde*-3 : 4 : 5-*trichlorophenylhydrazone* (IV) separated when 2·5 g. of bromine (1 mol.) were added to 5 g. (1 mol.) of *o*-nitrobenzaldehyde-3 : 4 : 5-trichlorophenylhydrazone suspended in 250 c.c. of warm acetic acid. It was recrystallised from this solvent, in which it is moderately easily soluble, and from which it separates in pale yellow needles, m. p. 170° (decomp.) (Found : Cl + Br, 43·8. $C_{13}H_7O_2N_3Cl_3Br$ requires Cl + Br, 44·0%).

1-3 : 4 : 5-*Trichlorophenyl*-3-o-*nitrophenyl*iso*diazomethane* (V) separated when a solution of ω-bromo-*o*-nitrobenzaldehyde-3 : 4 : 5-trichlorophenylhydrazone in benzene was shaken with concentrated aqueous ammonia. It is sparingly soluble in benzene, chloroform, or acetic acid, and separates from these solvents in compact, yellow plates, which explode at 151° (Found : Cl, 31·2. $C_{13}H_6O_2N_3Cl_3$ requires Cl, 31·1%).

1-p-*Chlorophenyl*-3-o-*nitrophenyl*iso*diazomethane* was prepared from *o*-nitrobenzaldehyde-*p*-chlorophenylhydrazone, without the

isolation of an intermediate ω-bromo-derivative. It separated as a yellow, crystalline mass when a solution of bromine (1 mol.) was added to a suspension of the hydrazone (1 mol.) and an excess (2 mols.) of sodium acetate in acetic acid. It crystallises from this solvent, in which it is moderately easily soluble, in bright yellow needles, which explode at 147° (Found : Cl, 12·9. $C_{13}H_8O_2N_3Cl$ requires Cl, 13·0%).

Action of Chlorine upon o-*Nitrobenzaldehydephenylhydrazone.*—Chlorination proceeds more cleanly in chloroform than in acetic acid. Its progress is accompanied by marked changes in the colour of the solution, which serve as a convenient guide when it is desired to arrest the process at some intermediate point.

A slow current of chlorine was passed into a cooled suspension of 5 g. of *o*-nitrobenzaldehydephenylhydrazone in 50 c.c. of chloroform, until the solid had dissolved to form a red solution. This on standing yielded dark red crystals, which after recrystallisation from alcohol melted at 192°, and proved to be *o*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone.

ω-*Chloro*-o-*nitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone* (IX).—In a second experiment the stream of chlorine was continued until the solution became dark brown. From this solution, on addition of an equal volume of cold alcohol, ω-*chloro*-o-*nitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone* separated. It crystallises from chloroform, in which it is moderately easily soluble, in compact, yellow prisms, m. p. 132° (Found : Cl, 31·0. $C_{13}H_8O_2N_3Cl_3$ requires Cl, 30·9%).

The same compound is more readily prepared by passing chlorine into a suspension of *o*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone in chloroform until the solid just dissolves, and then adding an equal volume of alcohol, when it separates in a fairly pure state.

A small quantity of the substance, when boiled for some time with an alkaline solution of potassium permanganate, yielded *o*-nitrobenzoic acid, m. p. 144°.

ω-Chloro-*o*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone, like the ω-bromo-compound, loses hydrogen halide when pyridine is added to its benzene solution or when it is shaken with ammonia. The product, 1-2 : 4-dichlorophenyl-3-*o*-nitrophenyl*iso*diazomethane (expl : 140°), is the same in both cases and has already been described.

ω-*Chloro*-o-*nitrobenzaldehyde*-2 : 4 : 6-*trichlorophenylhydrazone* (X).—In a third experiment the passage of chlorine into the suspension in chloroform of *o*-nitrobenzaldehydephenylhydrazone was continued until no more was absorbed, and the colour of the solution had changed to a light brown. The excess of chlorine was evaporated off, and an equal volume of cold alcohol added, when ω-*chloro*-o-

nitrobenzaldehyde-2 : 4 : 6-*trichlorophenylhydrazone* separated as a yellow, crystalline solid. Yield from 5 g. of the original hydrazone, 4·5 g. It dissolves easily in chloroform or benzene, but is sparingly soluble in ligroin. It crystallises from benzene–ligroin in fine, yellow needles, m. p. 107° (Found: Cl, 37·5. $C_{13}H_7O_2N_3Cl_4$ requires Cl, 37·5%).

A small quantity when boiled for 3 hours with alkaline potassium permanganate solution yielded *o*-nitrobenzoic acid, m. p. 144°.

The same compound was prepared in a similar manner by the action of chlorine upon *o*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone.

ω-Chloro-*o*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone when dissolved in benzene and shaken with aqueous ammonia was converted into 1-2 : 4 : 6-trichlorophenyl-3-*o*-nitrophenyl*iso*diazomethane, which separated from the solution in almost theoretical quantity. This exploded at 163° and was identical with the compound similarly obtained from ω-bromo-*o*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone (p. 2412).

The ω-halogeno-*o*-nitrobenzaldehydephenylhydrazones described here all yield deep green colorations when a trace of an oxidising agent (nitric acid or ferric chloride) is added to their solutions in strong sulphuric acid. The *iso*diazomethane derivatives dissolve in sulphuric acid, giving yellow solutions which are unaffected by the addition of oxidising agents.

Both the ω-halogeno-*o*-nitrobenzaldehydephenylhydrazones and their *iso*diazomethane derivatives are decomposed by alcoholic potash, yielding as one of the products a halogen-substituted benzene, *e.g.*, 1-2 : 4 : 6-trichlorophenyl-3-*o*-nitrophenyl*iso*diazomethane yields 1 : 3 : 5-trichlorobenzene. A similar decomposition is effected by ammonia in *alcoholic* solution. The course of these reactions is at present under investigation.

THE QUEEN'S COLLEGE, OXFORD. [*Received, July 17th*, 1925.]

CCCXXVIII.—*The Isomerism of the Oximes. Part XXIII. Acyl Derivatives.*

By OSCAR L. BRADY and GERALD PATRICK MCHUGH.

IN this series of papers a considerable amount of work has been published on the various acyl derivatives of the aldoximes (see particularly J., 1913, **103**, 1613; 1916, **109**, 650; 1923, **123**, 1190, 2163; 1924, **125**, 1087; this vol., p. 844), and the object of the present communication is to fill in certain gaps and to summarise the position.

The action of benzoyl chloride on the α-aldoximes * has been studied by Minunni and his co-workers (*Gazzetta*, 1892, **22**, ii, 166; 1896, **26**, i, 456) and by Forster and Judd (J., 1910, **97**, 256). The former prepared the benzoyl derivatives from the α-aldoximes by treatment with benzoyl choride in ethereal solution, the latter tried to prepare the isomeric benzoyl derivatives from β-benzaldoxime and *p*-triazo-β-benzaldoxime by avoiding the presence of hydrogen chloride, which would be likely to cause inversion (compare the acetyl-β-aldoximes). They were, however, unsuccessful, both isomerides yielding the same benzoyl derivative. The action of benzoyl chloride on a solution in excess of sodium hydroxide of a number of other α-aldoximes has been investigated and in every case a benzoyl derivative was obtained, which, on hydrolysis with alkali, regenerated the original oxime. It had previously been found that benzoyl chloride converts the otherwise stable β-cinnamaldoxime and *o*-methoxy-β-cinnamaldoxime into α-benzoyl derivatives from which the α-oximes could be obtained by alkaline hydrolysis (Brady and Thomas, J., 1922, **121**, 2104; Brady and Grayson, J., 1924, **125**, 1419). This reaction is apparently a general one and it has been found that benzoylation by the Schotten-Baumann method converts β-benzaldoxime, *o*-, *m*-, and *p*-nitro-, *p*-methoxy-, and 3 : 4-methylenedioxy-β-benzaldoximes into the corresponding α-benzoyl derivatives. Similar results were obtained by benzoylating in pyridine solution with benzoylpyridinium chloride in spite of all precautions to avoid isomeric change. These results are somewhat remarkable, since ethyl chloroformate with an alkaline solution of the β-aldoximes invariably gave the nitrile, and acetylpyridinium chloride with a pyridine solution of the β-aldoximes also gave the nitrile.

The action of keten on the aldoximes promised to be of interest, since the behaviour of phenylcarbimide in giving inversion of configuration (Brady and Dunn, J., 1916, **109**, 650) suggested that keten, also an additive reagent, might act upon the α-aldoxime to give the acetyl-β-oxime. This expectation was, however, not realised, the α-aldoximes giving acetyl-α-aldoximes. With β-aldoximes and keten, the acetyl compound could not be isolated in a pure state, but treatment of the crude product with sodium hydroxide gave the corresponding nitrile, indicating the presence of the acetyl-β-aldoxime. The acetyl-β-aldoximes are very sensitive to traces of

* α-Aldoximes are those which on treatment with acetic anhydride and sodium carbonate give acetyl derivatives which regenerate the oxime on alkaline hydrolysis; β-aldoximes, those which give the nitrile under these conditions; α-acyl derivatives, those which on alkaline hydrolysis give the α-aldoxime; and β-acyl derivatives, those which give the nitrile (compare Brady and Bishop, this vol., p. 1357).

acid, being thereby converted into the acetyl-α-aldoxime, and it was possible that in the first case traces of hydrogen bromide were carried over by the keten; if, however, this had been the case, one would have expected a similar result when the β-aldoximes were employed, whereas here there was no doubt that the acetyl-β-aldoxime was formed.

If keten added to the C:N and N:O double bonds in the tautomeric form of the oximes, RCH:NH:O, in a manner similar to that suggested for phenylcarbimide (J., 1916, **109**, 659), an aryl*iso*oxazolidone (I) would be formed :

$$\begin{matrix} R\cdot CH \\ \| \\ HN{:}O \end{matrix} + \begin{matrix} CH_2 \\ | \\ CO \end{matrix} \longrightarrow \text{(I.)} \begin{matrix} R\cdot CH{-}CH_2 \\ | \quad | \\ HN{-}O{-}CO \end{matrix} \longrightarrow \begin{matrix} R\cdot CH \\ \| \\ N\cdot O\cdot CO\cdot CH_3 \end{matrix}$$

This might be expected to tautomerise to the acetylaldoxime, or to split off acetic acid and give the nitrile in a similar manner to the γ-alkyl*iso*oxazoles (II) (Claisen, *Ber.*, 1903, **36**, 3672).

$$\text{(II.)} \begin{matrix} R\cdot C{-}{-}CH \\ \| \quad | \\ N{-}O{-}CH \end{matrix} \xrightarrow{KOH} RCN + CH_3\cdot CO_2K.$$

A compound of this nature was described by Posner (*Annalen*, 1912, **389**, 97), who obtained γγ-diphenyl*iso*oxazolidone (III) by the action of hydroxylamine on β-phenylcinnamic ester; this compound might be formed by the action of keten on the tautomeric form of diphenylketoxime, and since, according to Posner, the compound was comparatively stable, there should have been no difficulty in isolating it; however, only acetyldiphenylketoxime was obtained in the reaction.

$$\begin{matrix} (C_6H_5)_2C \\ \| \\ HN{:}O \end{matrix} + \begin{matrix} CH_2 \\ | \\ CO \end{matrix} \longrightarrow \begin{matrix} (C_6H_5)_2C{-}{-}CH_2 \\ \| \quad | \\ HN{-}O{-}CO \end{matrix} \text{(III.)}$$

The acetyl-β-aldoximes have been described by Hantzsch (*Ber.*, 1891, **24**, 38; *Z. physikal. Chem.*, 1894, **13**, 509), who gives three general methods for their preparation, but, with the exception of acetyl-β-benzaldoxime, no experimental details for the individual compounds. His methods have been tried with four β-aldoximes, but our products differ considerably from his and could not be obtained free from unchanged oxime. Hantzsch publishes no analyses of the compounds other than acetyl-β-benzaldoxime and we are not convinced that other acetyl-β-aldoximes have, as yet, been obtained in the pure state.

In connexion with the inversion of configuration brought about by phenylcarbimide, the action of phenylcarbamyl chloride on the sodium salts of the α-aldoximes has been investigated; here the carbanilino-derivative of the α-oxime was obtained, there being no indication of the formation of the corresponding β-derivative.

Table I summarises the principal results which have been obtained in this series of investigations, but it is a matter of some difficulty to interpret them; α indicates that the acyl derivative formed in the reaction, on hydrolysis with sodium hydroxide, regenerates the α-aldoxime; β, that the acyl derivative, on alkaline hydrolysis, gives the nitrile; N indicates that the nitrile is formed; A, the aldehyde.

TABLE I.

Oxime.	Acetic anhydride.	Benzoyl chloride.	Diphenylcarbamyl chloride.	Diethylcarbamyl chloride.	Phenylethylcarbamyl chloride.	Ethyl chloroformate.	2:4-Dinitrochlorobenzene.	2:4:6-Trinitrochlorobenzene.	Phenylcarbimide.	α-Naphthylcarbimide.
Benzaldoxime	α	α	β	—	α	α	β	β	α + β	α
,, ...	β	α	β	—	—	N	A	A + N	β	β
o-Nitrobenzaldoxime	α	α	β	—	—	β	β	β	α*	—
,,	β	α	β	—	—	N	A	A + N	β	—
m-Nitrobenzaldoxime	α	α	β	α	α	α	β	β	α + β	α
,,	β	α	β	—	—	N	A	A + N	β	β
p-Nitrobenzaldoxime	α	α	β	β	β	β	β	β α + β		α
,,	β	α	β	β	β	N	A	A + N	β	β
p-Methoxybenzaldoxime	α	α	β	—	—	β	β	β	α + β	α
p-Methoxybenzaldoxime	β	α	—	—	—	N	A	A + N	β	β
3 : 4-Methylenedioxybenzaldoxime	α	α	—	—	α	β	β	β	α + β	α
3 : 4-Methylenedioxybenzaldoxime	β	α	—	—	—	N	A	A + N	β	β
Cinnamaldoxime	α	α	—	—	—	α	β	β	α*	α
,, ...	β	α	—	—	—	N	A	A + N	β	β
o-Methoxybenzaldoxime	α	α	β	—	—	α	β	β	α*	α
p-Dimethylaminobenzaldoxime	α	α	β	—	—	α	β	β	β	α

* In these cases the carbanilino-compound separated very slowly and isomeric change of any β-isomeride formed may have occurred.

It will be noticed that *o*-methoxybenzaldoxime and *p*-dimethylaminobenzaldoxime, which are known only in the α-form, give, in certain cases, derivatives which apparently have the β-configuration. The main problems, however, that have to be considered are: (1) How far it is justifiable to assume that all acyl derivatives which on alkaline hydrolysis give the nitrile have a similar configuration? (2) If the above assumption is correct, why one reagent, *e.g.*, ethyl chloroformate, brings about inversion of some oximes but not of others, whereas another similar reagent, diphenylcarbamyl chloride, always brings about inversion, and a third, benzoyl chloride, never. (3) Why phenylcarbimide causes inversion, but α-naphthylcarbimide does not do so. (4) Why benzoyl chloride is unique in yielding, with aqueous sodium hydroxide solutions of the β-aldoximes,

the benzoyl derivatives of the α-oxime rather than that of the β-oxime or the nitrile. (5) The nature of the very unstable, yellow carbanilino- and α-naphthylcarbamyl compounds which are frequently the first products of the action of the carbimides on the β-aldoximes (Goldschmidt and van Rietschoten, *Ber.*, 1893, **26**, 2087; Brady and Thomas, J., 1922, **121**, 2105; see also experimental part).

In connexion with the first point, adopting the new configuration of the aldoximes (Brady and Bishop, *loc. cit.*), the stereoisomeric acyl derivatives may be represented :

(IV.) $\begin{matrix} R\cdot CH \\ \| \\ N\cdot O\cdot COR' \end{matrix}$ Acyl derivative of α-oxime.

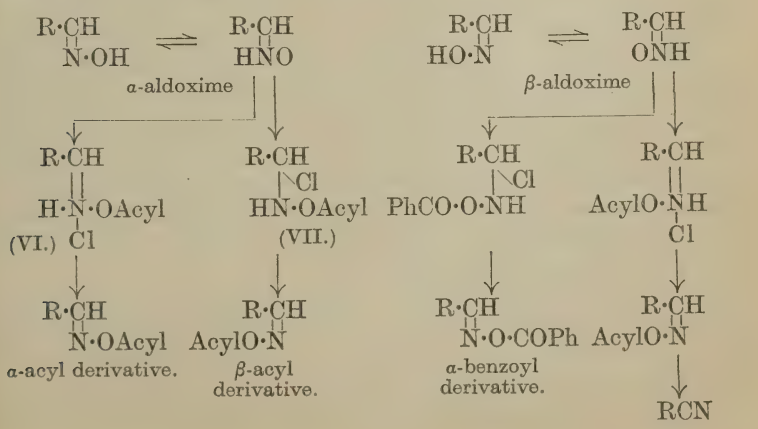
$\begin{matrix} R\cdot CH \\ \| \\ R'CO\cdot O\cdot N \end{matrix}$ (V.) Acyl derivative of β-oxime.

In normal cases, on alkaline hydrolysis, *trans*-elimination of acid will occur, (IV) regenerating the oxime and (V) giving the nitrile, but it is conceivable that in special cases *cis*-elimination of acid might readily take place and (IV) here give the nitrile. Consequently it might be argued that the carbethoxy-compounds obtained from *p*-methoxy-, 3 : 4-methylenedioxy-, *o*- and *p*-nitro-α-benzaldoximes have the same configuration (IV) as these oximes but that here *cis*-elimination of the acid readily occurs. Against this view, however, are the facts, first, the same carbethoxy-compounds were obtained from the β-aldoximes and secondly, the carbethoxy-compound obtained from *p*-nitro-α-benzaldoxime on boiling with alcohol gave a second carbethoxy-derivative, which behaved in a normal manner on hydrolysis, regenerating the original α-aldoxime; on the above hypothesis, this would indicate a change from configuration (IV) to configuration (V) and a reversal on hydrolysis. The first change is unlikely in view of the well-established reverse tendency, whilst if the latter contingency be admitted, the whole problem of oxime configuration would be thrown into indescribable confusion.

Another possibility is that in certain cases *N*-acyl derivatives are formed on the analogy of the *N*-ethers and that the carbethoxy-compounds prepared from *p*-methoxy-, 3 : 4-methylenedioxy-, *o*- and *p*-nitro-α-benzaldoximes, which on hydrolysis give the nitrile, should be represented as $R\cdot CH{:}N(:O)\cdot CO_2Et$, the effect of heating the carbethoxy-compound from *p*-nitro-α-benzaldoxime being the transference of the carbethoxy-group from N to O; against this, however, must be placed the nature of the absorption spectrum of *N*-derivatives, which does not accord with that of these carbethoxy-compounds. Moreover, one would then have to regard as *N*-acyl derivatives the diethylcarbamyl and phenylethylcarbamyl com-

pounds obtained from *p*-nitro-α-benzaldoxime, differentiating these from the diphenylcarbamyl derivatives; if the latter class are included, the dinitrophenyl- and trinitrophenyl-compounds, prepared from the α-aldoximes, would have to follow, but the action of 2 : 4-dinitrochlorobenzene and picryl chloride on the β-aldoximes is quite abnormal, the only explanation that appears possible being that it is in this case that an *N*-substituted compound is formed which is too unstable to be capable of free existence (Brady and Truszkowski, J., 1924, **125**, 1087; Brady and Klein, this vol., p. 844). In addition, the *N*-methyl ethers of the aldoximes are readily hydrolysed by alkali, not to the nitrile, but to the aldehyde. The idea that all acyl derivatives which give nitriles on hydrolysis are *N*-substituted compounds cuts at the very basis of the Hantzsch-Werner hypothesis and is difficult to maintain for other reasons, some of which have been given in previous papers. There seems, therefore, every reason to suppose that all acyl derivatives which on hydrolysis give the nitrile have the same configuration.

The application of the octet theory, although it suggested the very complicated nature of the electron changes which probably occur during acylation, did not elucidate the problem and after a careful consideration of many possible hypotheses, including an ionisation theory, we are still unable to advance any view that fits the facts better than that suggested by Dunn and one of us (J., 1916, **109**, 650). The new configuration being adopted, and the aldoximes being regarded as tautomeric, the acyl halide can add on in two ways, either at the N:O double bond (VI) or at both the C:N and N:O double bonds (VII); removal of hydrogen chloride produces no change in configuration in the first case, but does so in the second; similarly, in the case of the β-aldoxime :



With the α-aldoximes, the method of addition is governed partly by the nature of the aryl group R, *e.g.*, in the case of the carbethoxy-compounds, and partly by the nature of the acyl halide, *e.g.*, diphenylcarbamyl chloride; with the β-aldoximes, it seems to be decided solely by the nature of the acyl chloride, benzoyl chloride being the only one, so far investigated, which adds on at both double bonds.

The arguments previously adduced for the formation of the carbanilino-compounds must still hold in general, but it seems more probable that the yellow compounds obtained by the action of arylcarbimides on β-oximes are formed by the addition of the carbimide at first to the C:N double bond only, (VIII) then undergoing tautomeric change, the group migrating to the O, giving (IX).

$$\begin{matrix} R\cdot CH \\ \| \\ ONH \end{matrix} \longrightarrow \text{(VIII.)} \begin{matrix} R\cdot CH\text{--}NR \\ | \quad | \\ O{:}NH\text{--}C{:}O \end{matrix} \longrightarrow \begin{matrix} R\cdot CH \\ \| \\ RNH\cdot CO_2\cdot N \end{matrix} \text{(IX.)}$$

The nitrone structure here suggested, as in the case of the *N*-ethers, would account for the colour (compare also Staudinger and Miescher, *Helv. Chim. Acta*, 1919, **2**, 554, for the addition of diphenylketen to ketoximes).

Experimental.

Action of Benzoyl Chloride on α-Aldoximes.—The α-aldoxime (3 g.) was dissolved in 2*N*-sodium hydroxide (100 c.c.), benzoyl chloride (3 g.) added, and the mixture well shaken and cooled; when the odour of the chloride had disappeared, the solid was collected, washed, and crystallised. The orientation of the product was determined in each case by hydrolysis with warm 2*N*-sodium hydroxide, when a clear solution was obtained and no ammonia evolved, indicating the absence of a nitrile produced from a β-derivative. From the solution carbon dioxide precipitated the α-oxime, which was identified by the method of mixed melting points, whilst hydrochloric acid subsequently gave benzoic acid. No indication of the presence of the acid corresponding to the oxime was obtained. Benzoyl-*o*-nitro-α-benzaldoxime, as is usually the case with derivatives of this oxime, underwent profound decomposition on warming with alkali, but when left in contact with 2*N*-sodium hydroxide at room temperature until a clear solution was obtained, it reacted normally.

Benzoyl-o-*nitro*-α-*benzaldoxime* separated from alcohol in pale greenish-white plates, m. p. 112° (Found: N, 10·2. $C_{14}H_{10}O_4N_2$ requires N, 10·3%), *benzoyl*-p-*nitro*-α-*benzaldoxime* from acetone in pale greenish-white, rectangular plates, m. p. 196° (Found: N, 10·4%), *benzoyl*-3 : 4-*methylenedioxy*-α-*benzaldoxime* from acetic acid

in white plates, m. p. 168° (Found : N, 5·3. $C_{14}H_{10}O_4N$ requires N, 5·2%), *benzoyl-o-methoxy-α-benzaldoxime* from alcohol in white plates, m. p. 96° (Found : N, 5·6. $C_{15}H_{13}O_3N$ requires N, 5·5%), and *benzoyl-p-dimethylamino-α-benzaldoxime* from acetone and water in greenish-white plates, m. p. 138° (Found : N, 10·3. $C_{16}H_{16}O_2N_2$ requires N, 10·4%).

In addition, the benzoyl derivatives of α-benzaldoxime, *m*-nitro-, and *p*-methoxy-α-benzaldoximes (Minunni and Corselli, *Gazzetta*, 1892, **22**, 164) were prepared in an analogous manner from the corresponding α-aldoximes, and their configuration determined by hydrolysing them to the α-aldoximes with 2*N*-sodium hydroxide.

Action of Benzoyl Chloride on β-Aldoximes.—β-Benzaldoxime, *o*-, *m*-, and *p*-nitro-, *p*-methoxy-, and 3 : 4-methylenedioxy-β-benzaldoximes were benzoylated in a similar manner to the α-derivatives. In each case the corresponding benzoyl-α-aldoxime was obtained, which was identified by a mixed melting point and by hydrolysis to the α-oxime. The benzoyl chloride was shaken with a little sodium hydroxide immediately before use, in case any acid in it should bring about conversion. The benzoylation was carried out at 0° and the products were washed with iced water. They were crystallised by dissolution in cold acetone and precipitation by the cautious addition of water in order to avoid isomeric change, which might be brought about by the use of hot solvents, but no indication of the formation of a β-isomeride was obtained. In another series of experiments β-benzaldoxime, *m*-nitro-, and 3 : 4-methylenedioxy-β-benzaldoxime were dissolved in dry pyridine and cooled to 0° ; a solution of the calculated amount of benzoyl chloride in dry pyridine at 0° was added, and the mixture kept at 0°. The product was poured on to crushed ice and extracted with ether, the extract washed, dried over sodium sulphate, and the ether evaporated at room temperature. In every case the benzoyl-α-aldoxime was obtained. Similar results were obtained at −23° (compare Forster and Judd, *loc. cit.*). Acetylation of β-aldoximes under similar conditions gives the nitrile, but no indication of the formation of this compound was obtained during the benzoylation. 3 : 4-Methylenedioxy-β-benzaldoxime (5 g.) was dissolved in dry ether, sodium (0·7 g.) dissolved in a minimum of alcohol added, the precipitated sodium salt collected, washed with dry ether, rapidly dried on a porous tile, suspended in dry ether, and the calculated amount of benzoyl chloride added. After 2 hours, the solution was filtered, and on evaporating the ether at room temperature benzoyl-3 : 4-methylenedioxy-α-benzaldoxime was obtained.

Action of Keten on α-Aldoximes.—The keten was prepared (Staudinger and Klever, *Ber.*, 1908, **41**, 594) by the action of zinc

filings on 50 g. of bromoacetyl bromide in 250 c.c. of dry ether in a current of hydrogen. Ether and keten distilled over and were passed directly into a dry ethereal solution of 1 g. of the oxime; this was then evaporated over solid sodium hydroxide in a continuously evacuated desiccator and the solid residue pressed on a tile. 3 : 4-Methylenedioxy-α-benzaldoxime gave a crude product which melted alone at 98—104°, at 102—104° when mixed with acetyl-3 : 4-methylenedioxy-α-benzaldoxime, and at 105° after one crystallisation from benzene. This was identified as the α-acetyl derivative by comparison with a specimen prepared by the action of acetic anhydride at 30° on 3 : 4-methylenedioxy-α-benzaldoxime followed by treatment with sodium carbonate solution. *Acetyl-3 : 4-methylenedioxy-α-benzaldoxime* crystallised from alcohol in fine, white needles, m. p. 105° (Found: N, 6·9. $C_{10}H_9O_4N$ requires N, 6·7%).

In the cases of *m*- and *p*-nitro-α-benzaldoximes the reaction was incomplete even after 24 hours, although the solution had still a strong odour of keten. Accordingly the ether was evaporated, and the crude product washed with a small amount of cold 2*N*-sodium hydroxide, which removed unchanged oxime, identified as the α-isomeride after precipitation with carbon dioxide. The residues, after drying on a tile, melted at 121° (*m*-compound; when mixed with acetyl-*m*-nitro-α-benzaldoxime, at 126°) and 124—129° (*p*-compound); in each case the pure acetylnitro-α-benzaldoxime was obtained after one crystallisation from alcohol.

In all three cases the crude product, on hydrolysis with warm 2*N*-sodium hydroxide, gave the corresponding α-oxime, no nitrile or acid being detected. This result and the melting points of the crude products indicate that no appreciable amount of acetyl-β-aldoxime had been formed and subsequently converted into the α-isomeride during crystallisation; for the former is immediately converted by cold sodium hydroxide into the nitrile and subsequently into the carboxylic acid.

Action of Keten on β-Aldoximes.—3 : 4-Methylenedioxy-β-benzaldoxime, when treated as above, gave after evaporation of the ether a viscous product which could not be crystallised. After hydrolysing with 2*N*-sodium hydroxide, saturating the solution with carbon dioxide, and extracting with ether, a small amount of 3 : 4-methylenedioxy-α-benzaldoxime was isolated, whilst on acidifying with hydrochloric acid and again extracting 3 : 4-methylenedioxybenzoic acid was obtained. From *m*-nitro-β-benzaldoxime, a crude product, m. p. 82—90°, was obtained; this was triturated with cold 2*N*-sodium hydroxide, and the residue identified as *m*-nitrobenzonitrile, formed from the β-acetyl derivative; the alkaline

solution, on treatment with carbon dioxide followed by ether extraction, gave *m*-nitro-α-benzaldoxime.

Action of Keten on Diphenylketoxime.—When diphenylketoxime was treated with keten, the ether solution on evaporation gave a mass of crystals, m. p. 72°, which after crystallisation from light petroleum gave pure acetyldiphenylketoxime, m. p. 74°. This was identified by comparison with a specimen obtained by the action of acetic anhydride on the ketoxime.

Acetyl Derivatives of β-Aldoximes.—Owing to the sensitivity of the acetyl-β-aldoximes, this work was carried out in a room free from acid fumes and illuminated by deep orange light only.

A solution of the β-aldoxime in a minimum of pure acetic anhydride was kept at room temperature for 5 minutes and then cooled to −20°; the solid was produced by scratching for some time. The suspension was poured on to a porous tile, and the solid crystallised by dissolving in dry benzene at room temperature and adding light petroleum slowly with constant scratching. The acetyl derivative thus produced was triturated with cold 2*N*-sodium hydroxide, kept for 5 minutes, and filtered. The solid residue was the nitrile; from the solution, yellow in the case of the nitro-compound, concentrated ammonium chloride precipitated the corresponding β-aldoxime. *o*-Nitro-β-benzaldoxime (m. p. 152°) gave *acetyl-o-nitro-β-benzaldoxime*, m. p. 73° (Found: N, 13·9. $C_9H_8O_4N_2$ requires N, 13·5%). The β-aldoxime recovered after trituration with sodium hydroxide had m. p. 146—149°. *m*-Nitro-β-benzaldoxime (m. p. 112°) gave a product, m. p. 96—98° (Hantzsch gives 75°) (Found: N, 14·2. Calc., N, 13·5%); the recovered β-aldoxime melted alone at 108—115°, and at 92° when mixed with the α-aldoxime. *p*-Nitro-β-benzaldoxime (m. p. 174°) gave a product, m. p. 96° (H. 75—76°) (Found: N, 14·4. Calc., N, 13·5%); the recovered β-aldoxime melted at 165—168°. 3 : 4-Methylenedioxy-β-benzaldoxime gave a product, m. p. 86° (H. 99°) (Found: N, 7·2. Calc., N, 6·7%); the recovered β-aldoxime melted at 135—138°.

No satisfactory results were given by the other methods described by Hantzsch (*Z. physikal. Chem.*, 1894, **13**, 509). The isolation of the β-aldoxime by treating with cold sodium hydroxide suggested that the supposed acetyl derivatives were contaminated with unchanged oxime. This was confirmed by the high percentage of nitrogen found. An alternative explanation is that the hydrolysis of the acetyl-β-oxime gave partly nitrile and partly β-oxime, the high analytical figures being due to contamination with nitrile. Judging from experience in the hydrolysis of other acyl-β-aldoximes, we think the second contingency the less likely.

Action of Ethyl Diazoacetate on Aldoximes.—Dry ethereal solutions

of *m*-nitro- and 3 : 4-methylenedioxy-α- and -β-benzaldoximes were treated with a slight excess of an ethereal solution of ethyl diazoacetate at room temperature for 48 hours. On removal of the solvent, the solutions of the α-aldoximes gave unchanged α-aldoxime, whilst those of the β-aldoximes gave a mixture of α- and β-aldoximes owing to isomeric change of the former into the latter.

Action of Phenylcarbimide on Aldoximes (compare Goldschmidt and others, *Ber.*, 1889, **22**, 3112; 1890, **23**, 2136; 1891, **24**, 2546; 1893, **26**, 2087; Beckmann, *ibid.*, 1890, **23**, 3321; Brady and Dunn, J., 1916, **109**, 650; Brady and Thomas, J., 1922, **121**, 2100).—3 : 4-Methylenedioxy-α-benzaldoxime (7 g.) in a minimum of dry ether was treated with phenylcarbimide (5 g.), the precipitate that formed at once was separated, pressed on a porous tile, and washed with dry ether; it then melted at 78° (decomp.). A portion was treated with alcohol under reflux for an hour. On cooling, a small amount of diphenylcarbamide crystallised; the alcoholic filtrate from this was evaporated to dryness, and the residue crystallised from benzene and light petroleum, *carbanilino*-3 : 4-*methylenedioxy*-α-*benzaldoxime* being obtained as a white, micro-crystalline powder, m. p. 104° (decomp.) (Found: N, 9·7. $C_{15}H_{12}O_4N_2$ requires N, 9·8%).

From another portion, carbanilino-3 : 4-methylenedioxy-α-benzaldoxime was isolated by a method analogous to that used by Brady and Dunn for the *m*-nitro-derivative (J., 1916, **109**, 670; compare *idem*, J., 1914, **105**, 2877). The remainder of the crude product was hydrolysed with 2*N*-sodium hydroxide, when 3 : 4-methylenedioxybenzoic acid and 3 : 4-methylenedioxy-α-benzaldoxime were obtained, the former preponderating. There was, therefore, no doubt that the crude compound was a mixture of the two carbanilino-derivatives. When 3 : 4-methylenedioxy-β-benzaldoxime was similarly treated with phenylcarbimide, the precipitated *carbanilino*-3 : 4-*methylenedioxy*-β-*benzaldoxime* formed greenish-white plates, m. p. 84° (decomp.) (Found: N, 9·9. $C_{15}H_{12}O_4N_2$ requires N, 9·8%). Attempts to crystallise the compound from various solvents invariably led to isomeric change, the melting point falling. On treatment with warm 2*N*-sodium hydroxide it was rapidly decomposed; the insoluble residue consisted of 3 : 4-methylenedioxybenzonitrile and no α-oxime was detected; more prolonged hydrolysis gave the acid and ammonia. Similar results were obtained by the action of phenylcarbimide (6 g.) on *p*-nitro-α-benzaldoxime (4 g.), the mixture being kept for 5 minutes before the precipitate was separated. The crude product (m. p. 88°) on hydrolysis gave a mixture of acid and α-oxime, and on boiling with alcohol gave carbanilino-*p*-nitro-α-benzaldoxime,

m. p. 148—150°. With *p*-methoxy-α-benzaldoxime, the crude product (m. p. 74°) on hydrolysis gave acid and α-oxime, and on boiling with alcohol, the pure carbanilino-*p*-methoxy-α-benzaldoxime, m. p. 103°. In the case of *o*-nitro-α-benzaldoxime the addition of phenylcarbimide did not cause rapid precipitation of the carbanilino-derivative, so the solution was kept in the dark, out of contact with moisture, for 24 hours. The precipitate then melted at 105° and after one crystallisation from light petroleum gave pure carbanilino-*o*-nitro-α-benzaldoxime, m. p. 119°. The crude product on hydrolysis gave the α-oxime but no acid and seemed to contain no carbanilino-*o*-nitro-β-benzaldoxime, any which might have been formed originally having probably undergone isomeric change owing to the long period of keeping.

o-Methoxy-α-benzaldoxime, treated in an analogous manner to the above, behaved similarly. The crude product (m. p. 106°) on recrystallisation from benzene and light petroleum gave *carbanilino-o-methoxy-α-benzaldoxime*, white needles, m. p. 107° (decomp.) (Found: N, 10·5. $C_{15}H_{14}O_3N_2$ requires N, 10·4%). Hydrolysis of the crude product gave *o*-methoxy-α-benzaldoxime but no *o*-methoxybenzoic acid.

Action of Phenylcarbamyl Chloride on the Sodium Salts of α-Aldoximes.—The behaviour of two oximes, *viz.*, *m*-nitro- and *p*-methoxy-α-benzaldoxime, was investigated. The oxime was dissolved in dry ether, the calculated quantity of sodium dissolved in the minimum of alcohol added, the precipitated sodium salt washed with dry ether, and dried for a week in the dark over solid sodium hydroxide in a vacuum. The finely powdered salt was suspended in dry ether, in a well-stoppered vessel, and freshly prepared phenylcarbamyl chloride (1 mol.) added. The mixture was kept for 2 hours, with occasional shaking, filtered, and the solid extracted with cold chloroform. The residue, after being washed with water to remove sodium chloride, contained a very small quantity of diphenylcarbamide. In the case of *m*-nitro-α-benzaldoxime the chloroform solution was diluted with light petroleum; the precipitate formed consisted of slightly impure carbanilino-*m*-nitro-α-benzaldoxime. Alkaline hydrolysis gave only the α-oxime and no *m*-nitrobenzoic acid. In the case of *p*-methoxy-α-benzaldoxime, the chloroform was removed by a current of dry air; the crude product (m. p. 99°) was carbanilino-*p*-methoxy-α-benzaldoxime, alkaline hydrolysis giving the α-oxime and no acid.

Diphenylcarbamyl-o-methoxy-β-benzaldoxime.—A solution of sodium (0·76 g.) in the minimum of absolute alcohol was added to a solution of *o*-methoxybenzaldoxime (5 g.) in dry ether, followed by a large excess of ether. The precipitated sodium salt was washed

with ether and dried in a vacuum over solid sodium hydroxide, suspended in dry chloroform with diphenylcarbamyl chloride (7·7 g.), and heated under reflux for 4 hours. The sodium chloride formed was separated, and the filtrate evaporated at room temperature. The oil was treated with 10 c.c. of 2*N*-sodium hydroxide and 10 c.c. of ether, the whole being well stirred together. The colourless crystals separating were collected, washed with a little ether, then with water, and dried in a vacuum. On crystallising from light petroleum to which about 10% of benzene had been added to increase the solvent action, *diphenylcarbamyl-o-methoxy-β-benzaldoxime* was obtained in small, colourless needles, m. p. 124° (decomp.) (Found : N, 8·2. $C_{12}H_{18}O_3N_2$ requires N, 8·1%). On hydrolysis with sodium hydroxide under reflux, ammonia was evolved, and diphenylamine and *o*-methoxybenzoic acid were isolated from the solution.

Action of Ethyl Chloroformate on α- and β-Cinnamaldoximes (compare Brady and McHugh, J., 1923, **123**, 1190).—α-Cinnamaldoxime (1 g.) was dissolved in 2*N*-sodium hydroxide (20 c.c.), and ethyl chloroformate (0·8 g.) added with cooling and shaking. The precipitate was washed with water, pressed on a tile, washed with a very little ether, and crystallised from benzene and light petroleum, when *carbethoxy-α-cinnamaldoxime* was obtained in pale yellow crystals, m. p. 64° (Found : N, 6·6. $C_{12}H_{13}O_3N$ requires N, 6·4%). On hydrolysis by heating on the water-bath for an hour with 2*N*-sodium hydroxide and saturating with carbon dioxide, the α-oxime was recovered. When β-cinnamaldoxime was treated under the same conditions with ethyl chloroformate, an uncrystallisable oil was obtained, which was identified as cinnamonitrile by its boiling point and by hydrolysis to ammonia and cinnamic acid.

Action of α-Naphthylcarbimide on α- and β-Cinnamaldoximes (compare Brady and Ridge, J., 1923, **123**, 2163).—α-Cinnamaldoxime in dry ether was mixed with an equal weight of α-naphthylcarbimide in a stoppered vessel; after 1 hour, glistening, pale yellow plates of *α-naphthylcarbamyl-α-cinnamaldoxime* separated, m. p. 152° (decomp.). Crystallisation from acetone and water did not alter the melting point (Found : N, 9·0. $C_{20}H_{16}O_2N_2$ requires N, 8·9%). Hydrolysis with hot 2*N*-sodium hydroxide for an hour gave α-naphthylamine, *s*-di-α-naphthylcarbamide, and α-cinnamaldoxime (see Brady and Ridge, *loc. cit.*, for a general method of separation).

To a solution of β-cinnamaldoxime in dry ether was added an equal weight of α-naphthylcarbimide. After keeping for 30 minutes, glistening, deep yellow plates were deposited which, after being washed with dry ether, consisted of *yellow α-naphthylcarbamyl-β-*

cinnamaldoxime, m. p. 125° (decomp.) (Found : N, 9·0. $C_{20}H_{16}O_2N_2$ requires N, 8·9%). This compound could not be crystallised. When it was dissolved in cold acetone, and water added cautiously, rectangular plates of *colourless α-naphthylcarbamyl-β-cinnamaldoxime* separated, m. p. 125° (decomp.) (Found : N, 8·9%) (compare Brady and Thomas, J., 1922, **121**, 2105, for similar behaviour with phenylcarbimide). A mixture of the yellow and white modifications still melted and decomposed at 125°, and both forms on hydrolysis with 2*N*-sodium hydroxide for an hour gave α-naphthylamine, *s*-di-α-naphthylcarbamide, ammonia, and cinnamic acid.

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CCCXXIX.—*The Isomerism of the Oximes. Part XXIV. 4-Methoxy-3-methyl-, 3-Nitro-4-methyl-, and Some ortho-Substituted Benzaldoximes.*

By OSCAR L. BRADY, ANTOINETTE N. COSSON, and ARTHUR J. ROPER.

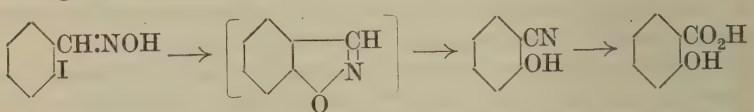
THIS communication is a continuation of those dealing with the influence of one or more substituents in the benzene nucleus on the formation of the unstable β-oxime (see this vol., p. 2415, for footnote explaining the nomenclature adopted) (Brady and Dunn, J., 1914, **105**, 821, 2409, 2872; 1915, **107**, 1858; 1916, **109**, 667; Wentworth and Brady, J., 1920, **117**, 1040; Brady and Truszkowski, J., 1923, **123**, 2434; Brady and Manjunath, J., 1924, **125**, 1060).

Some doubt exists how far substitution in the ortho-position with respect to the oximino-group prevents the formation of the β-isomeride; *o*-nitrobenzaldoxime, 2 : 4-dimethyl- and 2-chloro-3-nitrobenzaldoximes have been prepared in two forms by the usual method, and *o*-chloro-β-benzaldoxime was obtained by Behrend and Nissen (*Annalen*, 1892, **269**, 390) by the action of alkalis on bisnitrosyl-*o*-chlorobenzyl and by McHugh and one of us (J., 1924, **125**, 547) by the action of ultra-violet light on the α-isomeride, but attempts to obtain it through the hydrochloride were unsuccessful (Dollfus, *Ber.*, 1892, **25**, 1923). Similarly, although 2 : 5-dimethyl-β-benzaldoxime was obtained by Scholl and Kačer (*Ber.*, 1903, **36**, 322) by the action of mercuric fulminate on *p*-xylene in presence of aluminium chloride, it could not be prepared from the α-oxime through the hydrochloride (Francesconi and Mundici, *Gazzetta*, 1902, **32**, ii, 467). Dollfus (*loc. cit.*) failed to convert *o*-methylbenzaldoxime into the β-form and many attempts to prepare the β-isomeride of *o*-methoxybenzald-

oxime under widely varying conditions have been made, but without success, by one of us and others; failure in the latter case is the more surprising since *p*-methoxy-β-benzaldoxime is exceptionally stable.

The behaviour of *o*-halogeno- and *o*-ethoxy-benzaldoximes has now been studied. *o*-Chloro- and *o*-bromo-α-benzaldoximes were converted into their β-isomerides through the hydrochloride under suitable experimental conditions, but no β-compound could be obtained from *o*-iodo- and *o*-ethoxy-α-benzaldoximes. It is notable that the β-isomerides of ortho-substituted compounds can in some cases be prepared only under special experimental conditions but that when obtained they do not appear to be unusually unstable. There seems, therefore, to be no justification for assuming that failure to obtain β-isomerides from certain aldoximes is due to excessive instability of that form, and we are of opinion that the explanation must be sought either in the constitution of the hydrochloride or in some influence hindering the rearrangement of the hydrochloride; this view is supported by the formation of β-derivatives from oximes known only in the α-form, *e.g.*, carbanilinodimethylamino-β-benzaldoxime (Brady and Dunn, J., 1914, **105**, 2877). In general, it may be said that ortho-substitution does not necessarily inhibit the formation of the β-isomeride, but produces a distinct hindering effect.

The action of alkalis on *o*-halogenobenzaldoximes has been investigated (compare Brady and Bishop, this vol., p. 1357). The results are given in the experimental section; the formation of salicylic acid from *o*-iodo-α-benzaldoxime probably takes place through the benz*iso*oxazole:



It is unfortunate that *o*-iodo-β-benzaldoxime could not be obtained, because we were unable to test further the results of Bishop and one of us on the relative ease of formation of the *iso*-oxazole ring from the two isomerides.

Experimental.

o-*Chloro*-α- and -β-*benzaldoximes*.—Solutions of hydroxylamine hydrochloride (12 g. in 200 c.c. of water) and sodium hydroxide (18 g. in 200 c.c. of water) were mixed with cooling, and *o*-chlorobenzaldehyde (20 g.) was added. After 10 minutes, the mixture was shaken with ether to extract impurities such as *o*-chlorobenzyl

chloride (which are frequently present in the aldehyde). The α-oxime was precipitated from the alkaline solution with carbon dioxide, crystallised from benzene, dissolved in concentrated hydrochloric acid, and the solution saturated with hydrogen chloride and poured slowly into a large excess of 2*N*-sodium carbonate with very vigorous stirring. The oxime thus precipitated was washed, rapidly dried (m. p. 62—96°) on a porous tile, dissolved in benzene, and light petroleum added; the β-oxime then crystallised, m. p. 101—103° (Behrend and Nissen, *loc. cit.*, give m. p. 98—102°, and Brady and McHugh, *loc. cit.*, 110°).

When a solution of the α-oxime in dry ether was saturated with hydrogen chloride, no precipitate appeared, but on scratching for a few minutes a *hydrochloride* separated as a white, crystalline powder, m. p. 108° (decomp.) (Found: Ionisable Cl, 17·9. $C_7H_7ONCl_2$ requires ionisable Cl, 18·5%). On decomposition with 2*N*-sodium carbonate this regenerated the α-oxime, and a similar result was obtained when boiling benzene was employed as solvent (compare Brady and Dunn, J., 1923, **123**, 1783).

o-*Bromo*-α-*benzaldoxime*.—The preparation of *o*-bromobenzaldehyde from *o*-bromotoluene by Etard's reaction having given very poor yields, the following, more satisfactory, method was used. Acetic anhydride (40 g.), glacial acetic acid (30 g.), concentrated sulphuric acid (15 g.), and *o*-bromotoluene (5 g.) were mixed cautiously in the order named, cooled to 0°, chromium trioxide (10 g.) in glacial acetic acid (30 g.) was slowly added, the temperature being kept below 10°, and the mixture was poured on to crushed ice. The solid produced, on crystallising from alcohol, gave o-*bromobenzylidene diacetate* in colourless crystals, m. p. 84—86° (Found: Br, 27·8. $C_{11}H_{11}O_4Br$ requires Br, 27·9%). The diacetate was boiled under reflux for 2 hours with concentrated hydrochloric acid, and the solution diluted and shaken with ether. The crude aldehyde isolated from the extract was oximated by the method described above for the *o*-chloro-compound; by crystallising the product from benzene, pure *o*-bromo-α-benzaldoxime was obtained, m. p. 102° (compare V. Meyer, *Ber.*, 1892, **25**, 2188). This was oriented in the usual way by means of acetic anhydride. *Acetyl*-o-*bromo*-α-*benzaldoxime* crystallises from light petroleum or from acetone and water in colourless plates, m. p. 66° (Found: N, 5·8. $C_9H_8O_2NBr$ requires N, 5·8 %).

o-*Bromo*-β-*benzaldoxime*.—A solution of *o*-bromo-α-benzaldoxime in chloroform was saturated with hydrogen chloride. No hydrochloride was precipitated, so the solution was added to excess of vigorously stirred 2*N*-sodium hydroxide, the alkaline layer separated and rapidly saturated with carbon dioxide. The precipitated oxime

was rapidly dried on a porous tile and crystallised from benzene, *o-bromo-β-benzaldoxime* being obtained in colourless needles, m. p. 126° (Found : N, 7·2. C_7H_6ONBr requires N, 7·0%). On treatment with acetic anhydride and sodium carbonate, this gave *o*-bromobenzonitrile, m. p. 51°. No conversion of the α- into the β-oxime was effected by dissolution in concentrated hydrochloric acid, etc. A solution of the α-oxime in ether saturated with hydrogen chloride gave, on scratching, a *hydrochloride* as a white, crystalline powder, m. p. 115° (decomp.) (Found : Cl, 15·3. $C_7H_7ONClBr$ requires Cl, 15·0%); this on decomposition with sodium carbonate regenerated the α-oxime.

o-*Iodo-α-benzaldoxime*.—Oxidation of *o*-iodotoluene by the method described above in the case of *o*-bromotoluene gave no *o*-iodobenzylidene diacetate. The aldehyde was therefore prepared by Friedländer's method (*Ber.*, 1884, **17**, 456) and the oxime by Patterson's (J., 1896, **69**, 1002). The latter, on treatment with ethereal hydrogen chloride, gave the hydrochloride as a yellow, crystalline powder, m. p. 100—102° (decomp.), but this on decomposition regenerated the original α-oxime. The other methods, described above, also failed to bring about conversion.

Action of Alkalis on o-*Halogenobenzaldoximes*.—*o*-Iodo-α-benzaldoxime was boiled for 2 hours under reflux with 20 times its weight of 30% sodium hydroxide. From a portion of the solution, acidified with dilute nitric acid, silver nitrate produced a copious precipitate of silver iodide. The remaining portion was acidified with dilute sulphuric acid and extracted with chloroform, the extract was washed with very dilute sulphurous acid to remove iodine and then evaporated. The solid residue on crystallisation from water gave salicylic acid, which was identified by direct comparison, by its reaction with ferric chloride, and by the formation of methyl salicylate. *o*-Chloro-α- and β-benzaldoximes and *o*-bromo-α-benzaldoxime gave no ionised halogen under the above conditions; *o*-bromo-β-benzaldoxime lost some halogen, the solution acidified with dilute nitric acid giving a very pronounced opalescence with silver nitrate, but the amount of decomposition was insufficient for salicylic acid to be isolated.

o-*Ethoxy-α-benzaldoxime*.—The oxime was prepared in the same way as *o*-chloro-α-benzaldoxime and crystallised from light petroleum; m. p. 58° (Löw, *Monatsh.*, 1891, **12**, 395). Attempts to obtain the β-isomeride by the methods here described were uniformly unsuccessful, the pure α-oxime being invariably recovered.

4-*Methoxy*-3-*methyl-α-benzaldoxime*.—Solutions of hydroxylamine hydrochloride (15 g. in 50 c.c. of water) and sodium hydroxide (20 g. in 150 c.c. of water) were mixed with cooling, and 4-methoxy-

3-methylbenzaldehyde (30 g.) was added. The aldehyde dissolved after 15 minutes' shaking, and after a further 30 minutes the solution was saturated with carbon dioxide; the oil thus precipitated slowly solidified. After being dried, it was crystallised by dissolving in light petroleum at 60° and cooling rapidly, when the oxime was obtained, m. p. 71° (Gattermann, *Annalen*, 1907, **357**, 355, gives m. p. 68—70°, but confesses to considerable difficulty in purifying his product). During the orientation of the compound in the usual way, *acetyl-4-methoxy-3-methyl-α-benzaldoxime* was obtained; it crystallised from light petroleum in white plates, m. p. 70° (Found: N, 7·0. $C_{11}H_{13}O_3N$ requires N, 6·8%).

4-Methoxy-3-methylbenzonitrile.—The α-oxime was boiled for 90 minutes under reflux with excess of acetic anhydride, and the solution thus obtained was cooled and poured into 2*N*-sodium carbonate. When the excess of anhydride had been decomposed, the mixture was placed on ice and left over-night; the oil had then solidified. A solution of the solid in absolute alcohol, on evaporating slowly, deposited *4-methoxy-3-methylbenzonitrile* in colourless needles, m. p. 51—52° (Found: N, 9·7. C_9H_9ON requires N, 9·5%). This was hydrolysed by boiling for 2 hours with 2*N*-sodium hydroxide, the solution cooled, acidified with hydrochloric acid, and the precipitate crystallised from alcohol, *4-methoxy-3-methylbenzoic acid* being thus obtained in small, colourless needles, m. p. 192° (Found: C, 64·9; H, 6·2. $C_9H_{10}O_3$ requires C, 65·1; H, 6·0%). This acid was also obtained, but in poor yield, by heating the aldehyde for an hour with ammoniacal silver nitrate, filtering the hot solution, and acidifying the filtrate with nitric acid.

4-Methoxy-3-methyl-β-benzaldoxime.—A solution of the α-oxime in warm chloroform was saturated during 15 minutes with hydrogen chloride. The precipitated hydrochloride, a white, crystalline powder, m. p. 171° (decomp.) (Found: Cl, 17·4. $C_9H_{12}O_2NCl$ requires Cl, 17·6%), was dissolved in excess of cold 2*N*-sodium hydroxide and a saturated solution of ammonium chloride added, when *4-methoxy-3-methyl-β-benzaldoxime* was precipitated; it crystallised from acetone and water in microscopic, colourless needles, m. p. 121° (Found: N, 8·3. $C_9H_{11}O_2N$ requires N, 8·5%). When its configuration was determined with acetic anhydride, this oxime gave 4-methoxy-3-methylbenzonitrile.

3-Nitro-4-methyl-α-benzaldoxime.—Hydroxylamine hydrochloride (8 g. in 25 c.c. of water) was mixed with sodium hydroxide (10 g. in 75 c.c. of water), and 3-nitro-4-methylbenzaldehyde (16 g.) in a minimum of warm alcohol added. After 2 hours, the solution was saturated with carbon dioxide, and the precipitate, after washing, crystallised from alcohol; *3-nitro-4-methyl-α-benzaldoxime* was then

obtained in pale yellow needles, m. p. 118—120° (Found : N, 15·6. $C_8H_8O_3N_2$ requires N, 15·6 %). Cold acetic anhydride and sodium carbonate solution gave *acetyl*-3-*nitro*-4-*methyl*-α-*benzaldoxime*, which separated from acetone and water in colourless crystals, m. p. 104° (Found : N, 12·5. $C_{10}H_{10}O_4N_2$ requires N, 12·2%). On hydrolysis, it regenerated the original oxime.

3-*Nitro*-4-*methyl*-β-*benzaldoxime*.—A solution of the α-oxime in warm dry chloroform, on saturation with hydrogen chloride, gave a white, crystalline precipitate of the *hydrochloride*, m. p. 140° (decomp.) (Found : Cl, 16·4. $C_8H_9O_3N_2Cl$ requires Cl, 16·6%). This was rapidly dissolved in 2*N*-sodium hydroxide (3 equivs.), and a saturated solution of ammonium chloride added ; the precipitate of 3-*nitro*-4-*methyl*-β-*benzaldoxime* separated from acetone and water in colourless crystals, m. p. 135° (Found : N, 15·5. $C_8H_8O_3N_2$ requires N, 15·6%). With acetic anhydride and sodium carbonate solution, this oxime gave 3-nitro-4-methylbenzonitrile.

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University College, London. [*Received, July 21st*, 1925.]

CCCXXX.—*The Periodic Crystallisation of Pure Substances.*

By Ernest Sydney Hedges and James Eckersley Myers.

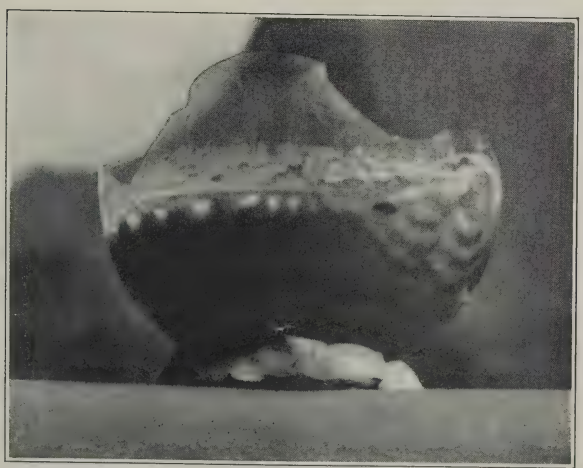
Several investigators have observed the production of periodic structures resembling the Liesegang phenomenon in the crystallisation of thin films of pure substances from a melt or from solution. Thus, Alexéev (*J. Russ. Phys. Chem Soc.*, 1906, **38**, 1120) reports that ethyl ethanetetracarboxylate, benzophenone, and coumarin crystallise in concentric zones when a thin layer of the molten substance is allowed to cool. Rhythmic crystallisation of sulphanilic acid–sulphuric acid mixtures, *p*-toluonitrile, salol, and methylsalicylic acid has formed the subject of an investigation by Schubert (*Kolloid-Z.*, 1924, **35**, 219), whilst Garner and Randall (J., 1924, **125**, 369) have shown that thin films of certain higher fatty acids crystallise in the form of waves. Vorländer and Ernst (*Z. physikal. Chem.*, 1919, **93**, 521) and Kägi (*Helv. Chim. Acta*, 1923, **6**, 264) observed crystallisation in concentric rings of other organic substances from a state of solution. The rhythmic crystallisation of thin films of molten sulphur has been investigated by Fischer-Treuenfeld (*Kolloid-Z.*, 1915, **16**, 109) and by Köhler (*ibid.*, 1915, **17**, 10). The cause of the phenomenon has been attributed by Alexéev (*loc. cit.*) to local alterations in surface tension due to the

Fig. 1.



The periodic crystallisation of benzoic acid from sulphuric acid–ethyl alcohol solution.

Fig. 2.



The effect is not confined to a surface film, but extends throughout the whole mass.

[*To face page* 2432.]

liberation of heat of crystallisation, and this view has also been urged by some more recent investigators.

Some cases are on record of the periodic crystallisation of inorganic salts from aqueous solution, the best-known instance being potassium dichromate (Miers, *Min. Mag.*, 1908, **15**, 39). Similar effects have been observed with sodium carbonate by Hofsäss (*Z. physikal. Chem.*, 1919, **93**, 754).

Experimental.

The present authors have carried out some experiments with thin films of solutions of chrome alum and of barium nitrate. In these cases, the best method of procedure is as follows: a drop of an aqueous solution of the substance saturated at room temperature is spread on a microscope slide, which is then warmed gently over a Bunsen flame and quickly transferred to the microscope. It is essential that the slide be carefully cleaned to facilitate spreading of the drop. The alternate periods of rapid and slow growth starting from the edge of the drop and producing corresponding rings of branched growths and geometrical crystals of potassium dichromate have been described by Miers (*loc. cit.*). With chrome alum, crystallisation proceeds much more slowly with the formation of a metastable, optically active, spherulitic form (compare Miers, *Min. Mag.*, 1906, **14**, 134). The bands consist of alternate zones of small and large spherulites. Crystallisation proceeds initially at a fairly rapid rate with the formation of a large number of small particles, and then at a slower rate with formation of a smaller number of large particles, the two speeds thereafter alternating. Similar observations were made with barium nitrate.

These observations are analogous to those of Hatschek (2nd Brit. Assoc. Colloid Report, 1918) on the distribution of particles with respect to size in rhythmic precipitation structures. In general, the periodic structure only appears in these cases when the film of liquid is very thin and the rate of crystallisation fairly rapid; the distance between the rings decreases for thinner films and with increasing rate of crystallisation. The view put forward by Miers is that crystallisation of the first ring takes place by inoculation when part of the solution reaches the labile state by cooling: as soon as this rapid growth has reduced the concentration of the solution in the immediate vicinity to the metastable condition, the crystals continue to grow slowly; in the meantime, the next ring of solution is becoming labile by evaporation and cooling and the rapid crystallisation recommences at some point. Such an explanation seems to meet the case of potassium dichromate, but it

is doubtful whether its applicability is universal. The authors would point out that at least in the case of chrome alum the periodicity is only observed when the metastable, spherulitic form appears, and this suggests a link with other types of physicochemical periodicity (Hedges and Myers, J., 1924, **125**, 604, 1282; this vol., pp. 445, 1013), which are associated with surfaces which are believed to be in a metastable state. It seems probable that periodic phenomena are a general characteristic of such metastable systems.

The foregoing instances are characterised by conditions where a small quantity of substance exhibits a large surface, but this does not appear to be essential for rhythmic crystallisation. The present authors have observed that benzoic acid crystallises in a very beautiful wave-form from mixtures of sulphuric acid and ethyl alcohol. This effect is well portrayed in Fig. 1. It is not a surface formation, but affects the whole mass of substance, the layers being arranged round the crystallisation nuclei like the coats of an onion. Fig. 2, which is another photograph of the same specimen taken from a different aspect, illustrates the solidity of the effect.

This phenomenon can be reproduced by warming 5 g. of benzoic acid with 12—20 c.c. of an equal-volume mixture of sulphuric acid and ethyl alcohol and setting aside to cool. The crystallisation starts from nuclei and spreads radially with constant decrease in the distance between successive rings. Although in almost all cases of rhythmic crystallisation the distance between successive rings is considerably less than a millimetre, in fact being often observable only by means of a lens, in the present case the effect is on a comparatively enormous scale and the rings in the specimen photographed were about a centimetre apart. Examination shows the layers to consist of closely packed crystals of benzoic acid separated by spaces containing mostly solution with some benzoic acid crystals sufficient to give rigidity to the whole. Crystallisation of benzoic acid from sulphuric acid or ethyl alcohol alone does not give rise to such periodic formations.

The authors wish to express their best thanks to Sir Henry A. Miers, F.R.S., in whose laboratory some of the experiments were carried out.

THE UNIVERSITY, MANCHESTER. [*Received, July* 31*st,* 1925.]

CCCXXXI.—*The Rotation-Dispersion of Optically Active Compounds. Dimethoxysuccinates and Pyridine.*

By Thomas Stewart Patterson and James Davidson Fulton.

Modern work on optical activity has disclosed, in general, the very important fact that if, under two entirely different sets of circumstances (temperature, concentration, solvent), the rotations for some particular colour, say sodium yellow, are the same, then the rotations for all the other colours also will be the same or very nearly the same, each to each. This is the lesson of the characteristic diagram, and it holds not merely for one and the same substance in different sets of circumstances, but also for derivatives of that active substance.

From the characteristic diagram we are thus able to foretell for a group of related compounds that if by varying the external conditions we can produce a certain rotation for one colour of light, the rotations for other colours will have certain definite values. But the characteristic diagram, unfortunately, does not indicate the physical conditions necessary to bring about a certain effect, or how they may be produced. Further, the characteristic diagram, although of a remarkably general character, is only an approximation, and, as far as can be judged at present, there are, probably, definite limits to its application. Thus for many substances, the rotation passes through a maximum or minimum value with change of temperature, and the data at present available are insufficient to show whether the rotation values on both sides of such a maximum fall upon a single characteristic diagram or not. It is clear that the difference between the rotation values for two colours of light—what may be called the dispersion—is directly proportional to either value, if calculated from the point of intersection for these two colours—the rational zero. Using the rational zero, a dispersion coefficient may be arrived at which shows very fair constancy under widely differing circumstances and may in future prove to be definitely characteristic of a particular substance or group of substances.

The experimental difficulties encountered in examining the rotation of an active substance over a wide range of temperature are considerable, and therefore only a comparatively short part of the T–R curves for most active compounds has been ascertained. It has been suggested, however, by one of us, that this difficulty can be at least partly overcome by piecing together T–R curves or solutions of the active compound in question, or derivatives of

it, just as a characteristic diagram is constructed by piecing together data of different kinds—the evidence being indeed just the same in both cases. The question, similar to that already referred to, then arises, as to whether the dispersion-coefficient derived from such T–R curves would have the same value as for the mother-substance, when calculated from the rational zero. It was with a view to collect further evidence of this kind that the work described below was undertaken.

For our purpose it is desirable to study substances the rotations of which vary as much as possible with change of external conditions. Some previous work had shown that benzyl tartrate has a fairly high rotation, and, moreover, that the maximum in the T–R curve lies at a moderate and easily ascertainable temperature (J., 1913, **103**, 148). We therefore thought it worth while to examine in the first place dibenzyl dimethoxysuccinate, hoping that its rotation would be both high and easily variable.

Dibenzyl dimethoxysuccinate was prepared from *d*-dimethoxysuccinic acid (J., 1901, **79**, 959) (1 mol.) by heating with pure benzyl alcohol (4 mols.) at 120° for about 16 hours and allowing the water formed to distil off. The excess of alcohol was removed under diminished pressure; the crude ester was washed with dilute sodium carbonate solution, taken up in chloroform, dried over calcium chloride, and distilled (yield 70%). It was slightly coloured and fairly mobile. Purified by careful distillation, it boiled at 180—190°/3 mm.; $n_D^{19°} = 1{\cdot}5321$ (Found: C, 66·8; H, 6·1. $C_{20}H_{22}O_6$ requires C, 67·0; H, 6·1%).

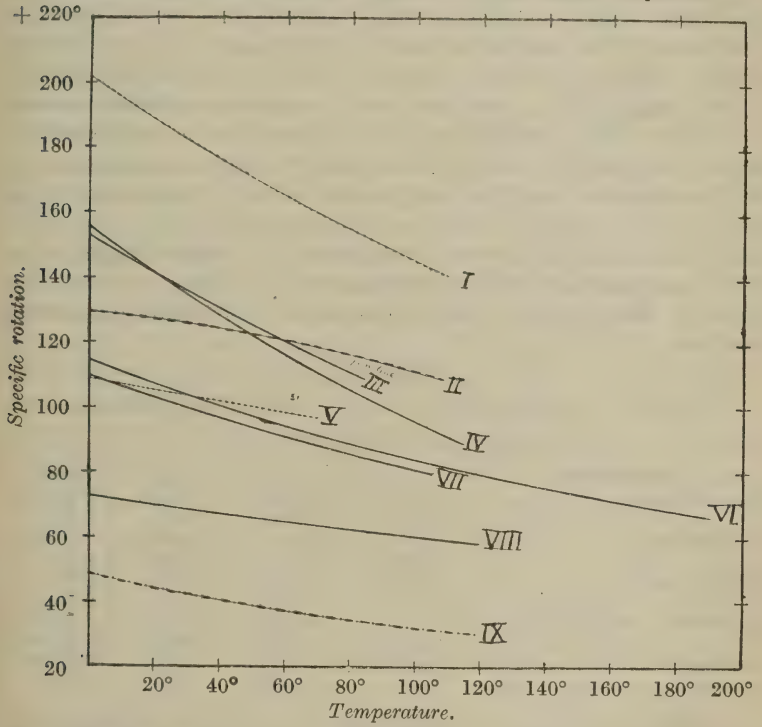
The rotation of this ester was examined for six different wavelengths of light at temperatures ranging from 0—100°. In the case of the homogeneous substance, the examination was continued up to 174°. The results are shown in Fig. 1, which gives the curves obtained for mercury green light alone. It will be seen that the specific rotation of the homogeneous benzyl dimethoxysuccinate, which has a high value of about 115° at zero, gradually falls to reach a value of 68° at a temperature of 180°, the appearance of the curve suggesting a maximum value at some temperature considerably below zero and a minimum value at a temperature possibly in the neighbourhood of 250°.

The influence of solvents upon this ester is also apparent from the diagram. Acetylene tetrabromide lowers the rotation of the ester considerably. *m*-Xylene lowers it only slightly. Nitrotoluene and quinoline both raise the rotation markedly. The general appearance of the curves is very similar to what has been observed already for the rotation of ethyl tartrate, but the displacement of a maximum or minimum value is not so obvious.

For purposes of comparison, the temperature–rotation curves of some other related compounds were examined. Benzyl tartrate (J., 1913, **103**, 176) in quinoline has a much lower rotation than benzyl dimethoxysuccinate, but the general appearance of the curve is similar. The rotation of methyl dimethoxysuccinic acid

FIG. 1.

Influence of solvents on the rotations of various related compounds.



I. d-*Dimethoxysuccinic acid in pyridine*, p = 7·8435. II. *Methyl* d-*dimethoxysuccinate in quinoline*, p = 5·5020. III. *Benzyl* d-*dimethoxysuccinate in quinoline*, p = 5·1758. IV. *Benzyl* d-*dimethoxysuccinate in* o-*nitrotoluene*, p = 4·860. V. d-*Dimethoxysuccinic acid in acetone*, p = 15·982. VI. *Benzyl* d-*dimethoxysuccinate* (*homogeneous*). VII. *Benzyl* d-*dimethoxysuccinate in* m-*xylene*, p = 6·6875. VIII. *Benzyl* d-*dimethoxysuccinate in acetylene tetrabromide*, p = 3·0660. IX. *Benzyl tartrate in quinoline*, p = 9·4489.

in acetone is considerably higher, but the curve is again of a similar form, the rotation gradually diminishing as the temperature rises. Dimethoxysuccinic acid dissolved in pyridine gives again a *T–R* curve of a similar form, the rotation, however, being much higher. Methyl dimethoxysuccinate dissolved in quinoline, shows, for all the colours of light examined, a behaviour suggesting a maximum

at a temperature in the neighbourhood of zero. It is clear, however, that any fundamental type of curve for these different compounds is not displaced to nearly so great an extent as is the curve for ethyl tartrate. All these curves, with the possible exception of that for methyl dimethoxysuccinate in quinoline, suggest that the *T–R* curve would rise to a maximum at lower temperatures than those examined. Homogeneous ethyl tartrate and the same ester dissolved in a number of solvents exhibited just the opposite behaviour. For homogeneous ethyl tartrate and for the ester in some solvents, the maximum is actually apparent. In some other solvents such as quinoline, pyridine, and benzaldehyde, the curves obtained suggest that a maximum value would lie, in these solvents, at a much lower temperature. On plotting on a characteristic diagram the results obtained with methyl dimethoxysuccinate in the homogeneous condition and in the solvents mentioned, it is found that the data lie fairly well upon straight lines, which for green and yellow light would intersect in the neighbourhood of a point corresponding to the rotation + 9°. Table I gives the necessary data and the rational dispersion coefficients calculated therefrom.

TABLE I.

Dispersion Coefficients for Benzyl *d*-Dimethoxysuccinate.

$[\alpha]_y/[\alpha]_g$ is the rational dispersion coefficient for the rational zero $[\alpha] = +9°$.

Physical state.	$t°$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_y/[\alpha]_g$.
Homogeneous	100°	72·72°	82·84°	0·8630
„	139·5	65·98	74·82	0·8659
In quinoline	0	134·9	154·59	0·8648
„	69·2	100·4	115·02	0·8621
In nitrotoluene	13·6	127·06	145·51	0·8648
„	72	95·13	108·25	0·8678
In acetylene tetrabromide ...	14	62·25	70·62	0·8642
„ „ ...	44·2	58·77	66·63	0·8636
In *m*-xylene	43·7	83·11	95·04	0·8614
„	69	76·73	87·31	0·8649

It will be observed that the coefficient is very constant, differences only occurring in the third decimal place. Its mean value is 0·8642.

In Table II are shown similar dispersion coefficients for the other substances which have been examined and it will be seen that the dispersion coefficient is slightly higher than before, having a mean value of about 0·876 when the values are calculated from a rational zero of + 9°.

The data of Tables I and II have reference, as will be apparent from Fig. 1, to a region of the *T–R* curves to the right of the maximum. It is of interest now to compare them with similar data for ethyl tartrate applying to *T–R* curves on the other side of

Table II.

Dispersion Coefficients for *d*-Dimethoxysuccinic Acid and for Methyl *d*-Dimethoxysuccinate.

$[\alpha]_Y/[\alpha]_G$ is the rational dispersion coefficient for the rational zero $[\alpha] = +9°$.

Physical state.	$t°$.	$[\alpha]_Y$.	$[\alpha]_G$.	$[\alpha]_Y/[\alpha]_G$.
d-Dimethoxysuccinic acid in pyridine	0°	180·96°	204·38°	0·8801
d-Dimethoxysuccinic acid in pyridine	69	142·37	161·24	0·8761
In acetone	12	94·00	106·29	0·8737
,,	30·5	91·96	103·75	0·8756
Methyl *d*-dimethoxysuccinate in quinoline	0	114·55	129·40	0·8766
Methyl *d*-dimethoxysuccinate in quinoline	67	105·67	119·39	0·8757

the maximum, namely, between temperatures of 40° and 140° (J., 1916, **109**, 119). The rational zero then found was + 7·92°, very close, therefore, to that (+ 9°) obtained from our present experiments. The mean value of the rational dispersion coefficient was 0·8660, again close to the values found above. Our results lend support, therefore, to the idea that even when the data are taken from *T–R* curves apparently on different sides of the maximum rotation, the rational dispersion-coefficient shows something like a real constancy.

Rotation of Nicotine.

Since it was not found possible to vary the rotation of the dimethoxysuccinates as much as we had hoped, we next undertook an examination of nicotine, the rotation of which is known to vary to some considerable extent, but has not hitherto been examined very completely in regard to change of colour, temperature, and concentration. Previous workers have given the following values for the constants of the homogeneous substance :

	$[\alpha]_D^{20°}$.	$d_{4°}^{20°}$.
Landolt ("Das Optische Drehungsvermögen," 2nd ed., 1898, p. 159)	161·55°	1·01101
Gennari (*Z. physikal. Chem.*, 1896, **19**, 130)	162·84	1·01071
Winther (*ibid.*, 1907, **60**, 563)	163·85	—
Jephcott (J., 1919, **105**, 105)	168·61	1·00925

The first three purified their nicotine by vacuum distillation only. In the last case the nicotine was purified by means of the zinc chloride double salt (Vohl, *J. pr. Chem.*, 1870, **2**, 331). We used 95% nicotine, purified it by preparation of the double salt with zinc chloride, decomposed this in sodium hydroxide, dried the nicotine over solid sodium hydroxide, and then distilled it under reduced pressure, using a Claisen flask with a long side arm, and a receiver of the type described in *J. Soc. Chem. Ind.*, 1924,

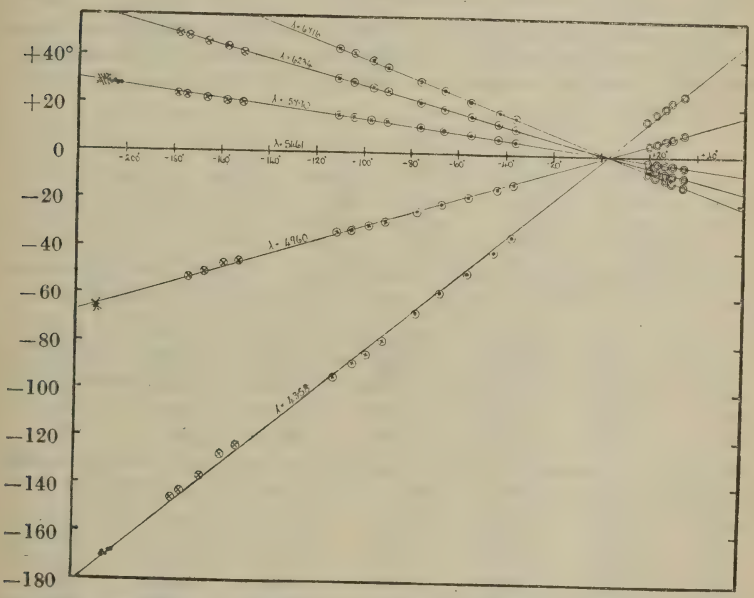
43, 283, thus avoiding completely any contact of the hot vapour or liquid with cork or rubber. A colourless, odourless liquid was obtained. Two separate preparations gave: (1) $[\alpha]_D^{20^\circ}$ 168·02°, $d_4^{20^\circ}$ 1·0095; (2) $[\alpha]_D^{20^\circ}$ 167·78°, $d_4^{20^\circ}$ 1·0100. The homogeneous substance was then examined for six colours of light over a range of temperature from 0—100°, in polarimeter tubes having a side arm to allow of expansion of the liquid. In order to prevent oxidation of the nicotine by air, a slow current of hydrogen was passed into the side arm. This proved entirely satisfactory; no coloration of the solution due to oxidation of the nicotine took place even at 100°, at which temperature oxidation in presence of air is extremely rapid. The data obtained, when plotted on a diagram, indicate that the change of rotation of nicotine with temperature is only slight, but the shape of the curves suggests the occurrence of a minimum at a temperature probably in the neighbourhood of 170° or thereabouts.

Nicotine was then examined in a number of solvents. *o*-Nitrotoluene as a solvent diminishes to some slight extent the rotation of nicotine, which is then almost unaffected by temperature change. In ethyl acetate, the rotation is depressed almost to the same extent, but not quite so much as in *o*-nitrotoluene, the temperature coefficient being again very small. α-Bromonaphthalene raises the rotation of nicotine, the temperature coefficient becoming somewhat greater at the same time—the rotation becomes more negative as the temperature rises. In quinoline, nicotine has a rotation at zero of — 152°. It falls steadily until at 100° the value is — 179°. This temperature–rotation curve is therefore quite in agreement with the others. Water raises the rotation of nicotine considerably, the value at zero being — 90°. Heating lowers the value much as in quinoline. Formamide also was used as a solvent, and in this case the rotation fell from — 35·6° at zero to — 77·5°. The formamide which we had used, however, was found to contain some formic acid; nevertheless, the curve obtained, as in many other cases, fits in along with those for the other solvents. We had hoped to raise the rotation of nicotine into the neighbourhood of $[\alpha] = 0^\circ$ in order to be able to examine a definite region of anomalous dispersion, but we have found no "inert" solvent which is capable of producing this effect. It is one of the interesting things, however, about the study of optical activity in solution that a solvent which combines chemically with the active compound behaves in very much the same way as one which would normally be regarded as indifferent; otherwise the characteristic diagram would be impossible. The increase in the rotation of the nicotine in the experiment just mentioned was doubtless partly

due to the formamide itself and partly due to the action of the formic acid which it contained. Solution of nicotine in an excess * of 3·2095*N*-aqueous sulphuric acid raised the rotation at 0° to 30·45°, and, on heating, the rotation gradually fell to 19·5° at 90°.

From the data for the various solutions examined, the characteristic diagram shown in Fig. 2 is obtained. It will be seen that the data obtained lie in a fairly satisfactory manner on the lines of the diagram. The data for the rotation of nicotine in excess of sulphuric acid are in agreement with the others. It seems clear

FIG. 2.



Characteristic diagram of nicotine in ◎ *sulphuric acid (excess),* ⊙ *formamide,* ⊕ *water,* ⊕ *quinoline,* ✳ *o-nitrotoluene,* • *homogeneous.*

from the diagram that if the rotation for green light could be made to take on a value in the neighbourhood of + 3° or 4°, the rotation dispersion would be visibly anomalous; the lines of the characteristic diagram intersect over a range. The behaviour of nicotine may therefore be said to be normal, inasmuch as it conforms to that observed for the large majority of—if not indeed for all—active compounds.

When dispersion coefficients, $[\alpha]_{5790}/[\alpha]_{5461}$, are calculated for nicotine from these data using the rational zero + 3°, the values found show a very fair constancy, the mean value being 0·8674.

* Such that all the nicotine existed, presumably, as sulphate.

The colours of light used were as follows :

	r_1.	r_2.	y.	g.	b.	v.
λ	6716·3	6234·3	5790·3	5460·7	4959·7	4358·3

Homogeneous benzyl d-*dimethoxysuccinate.* Densities determined : 1·1730 at 16·4°; 1·1551 at 41°; 1·1320 at 70·75°; 1·1064 at 100°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·1813	72·83°	85·16°	100·6°	114·17°	148·6°	193·3°
16·3	1·1732	69·91	80·25	94·99	108·05	135·5	181·2
44·4	1·1523	62·29	73·42	86·14	98·54	123·8	166·1
70·5	1·1324	56·99	68·08	79·65	90·20	114·1	152·7
100	1·1064	52·40	61·64	72·72	82·84	104·0	139·8
139·5	1·0685	47·09	55·80	65·98	74·82	93·84	127·5
174·5	1·0321	43·31	51·45	60·32	68·58	86·21	117·6

Benzyl d-*dimethoxysuccinate in quinoline,* $p = 5·1758$. Readings for some colours could not be taken at 100° owing to the darkening of the quinoline in solution. Densities determined : 1·0982 at 17·5°; 1·0740 at 48·5°; 1·0511 at 76°; 1·0312 at 100°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·1148	97·05°	114·3°	134·9°	154·6°	—	—
15·2	1·1020	90·64	105·3	126·6	142·9	178·8°	243·9°
44·2	1·0775	80·33	93·96	108·7	128·0	158·4	216·1
69·2	1·0566	72·97	84·30	100·4	115·0	142·0	198·8
100	1·0312	67·66	73·69	—	—	—	—

Benzyl d-*dimethoxysuccinate in nitrotoluene,* $p = 4·860$. Densities determined : 1·1682 at 16·7°; 1·1413 at 43·4°; 1·1150 at 70·7°; 1·0874 at 100°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.
0°	1·1843	98·51°	115·2°	137·0°	155·5°	197·0°
13·6	1·1709	90·50	107·0	127·0	145·5	184·0
43·5	1·1411	79·13	93·2	109·0	124·2	158·4
72	1·1139	68·53	80·4	95·13	108·3	137·1
100	1·0874	61·12	71·2	83·45	95·8	119·0

Benzyl d-*dimethoxysuccinate in acetylene tetrabromide,* $p = 3·066$. Densities determined : 2·8405 at 16·2°; 2·7853 at 42°; 2·7184 at 72·8°; 2·6651 at 98·8°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_v$.
0°	2·8755	47·18°	53·99°	63·18°	72·48°	118·2°
14·0	2·8452	45·40	53·73	62·25	70·62	116·2
44·2	2·7804	43·46	49·74	58·77	66·63	111·6
70·6	2·7238	40·59	47·42	55·92	63·34	105·4
98·8	2·6651	38·67	44·79	53·24	60·46	100·8

Benzyl d-*dimethoxysuccinate in* m-*xylene,* $p = 6·6875$. Densities determined : 0·8865 at 14·2°; 0·8630 at 42·2°; 0·8375 at 71°; 0·8122 at 99°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
16·9°	0·8843	68·91°	77·68°	91·10°	103·5°	131·8°	175·3°
43·7	0·8614	60·22	70·31	83·11	95·04	120·7	160·0
69	0·8392	55·13	64·82	76·73	87·31	111·4	147·7
98·7	0·8126	50·47	59·58	70·39	80·28	102·4	135·4

d-*Dimethoxysuccinic acid in pyridine,* $p = 7·8435$. Densities determined : 1·0137 at 15°; 0·9865 at 41·8°; 0·9621 at 66·7°; 0·9293 at 98·7°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·0287	129·9°	152·8°	181·0°	204·4°	255·3°	336·3°
14·8	1·0140	122·6	143·6	170·1	192·0	241·2	318·9
46·4	0·9819	111·4	130·1	151·3	172·6	218·0	287·8
69	0·9592	103·1	120·2	142·4	161·2	201·1	268·4
99	0·9293	92·8	110·0	128·2	146·1	184·0	243·5

d-*Dimethoxysuccinic acid in acetone*, $p = 15{\cdot}982$. Densities determined: 0·8558 at 21·5°; 0·8433 at 33°; 0·8327 at 42·8°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.
0°	0·8787	70·08°	81·82°	95·36°	108·5°
12	0·8656	70·24	80·08	94·00	106·3
30·5	0·8459	68·15	76·52	91·96	103·8
46·6	0·8283	65·95	73·12	88·98	100·8

Methyl d-*dimethoxysuccinate in quinoline*, $p = 5{\cdot}502$. Densities determined: 1·1026 at 14°; 1·0804 at 40·7°; 1·0582 at 68·3°; 1·0326 at 100·2°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_v$.
0°	1·1138	84·04°	97·74°	114·6°	129·4°	211·5°
13·5	1·1030	83·54	97·05	114·0	129·4	211·7
36·3	1·0844	81·79	94·69	111·0	125·9	208·5
67	1·0595	77·36	88·51	105·7	119·4	198·0
99·6	1·0332	—	80·92	98·2	110·8	unreadable

Benzyl tartrate in quinoline, $p = 9{\cdot}4489$. Densities determined: 1·1080 at 17°; 1·0878 at 40·2; 1·0627 at 72°; 1·0408 at 98·9°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.
0°	1·1213	31·34°	37·79°	43·56°	48·88°
13·5	1·1103	29·92	34·60	40·51	45·58
48·8	1·0818	25·26	30·46	34·89	38·63
74·2	1·0610	21·95	27·73	31·69	34·86
98·9	1·0408	21·57	25·04	30·29	32·15

Nicotine in formamide solution. The formamide contained some formic acid and caused a rise in rotation in the absolute sense from that obtained with pure formamide, $p = 18{\cdot}5040$. Densities determined: 1·1328 at 14·9°; 1·1061 at 50·8°; 1·0877 at 73·7°; 1·0660 at 99·3°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·1433	−20·99°	−25·57°	−30·77°	−36·30°	−49·35°	−73·88°
16·0	1·1325	26·01	30·97	37·36	43·66	58·89	86·99
44·6	1·1103	33·29	39·52	47·16	55·15	73·25	106·0
70·4	1·0899	39·82	47·90	56·72	66·25	87·12	124·8
99	1·0665	47·68	56·50	66·43	76·87	102·1	144·1

Solution of nicotine in o-*nitrotoluene*, $p = 4{\cdot}7337$. Densities determined: 1·1582 at 15·7°; 1·1322 at 43°; 1·1024 at 75°; 1·0789 at 99°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.
0°	1·1733	−128·4°	−153·7°	−184·1°	−211·0°	−277·3°
14·1	1·1598	129·4	154·5	182·1	211·0	278·3
40·8	1·1346	130·7	154·3	182·7	211·1	277·2
74·4	1·1025	130·6	154·7	182·6	211·4	277·6
99·2	1·0878	129·9	153·9	182·2	210·4	—

Solution of nicotine in quinoline, $p = 9{\cdot}1365$. Densities determined: 1·0888 at 15·3°; 1·0626 at 48·9°; 1·0413 at 75·2°; 1·0217 at 99·4°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·1010	−93·75°	−110·3°	−131·3°	−151·3°	−197·2°	−274·9°
17	1·0878	96·59	114·8	137·1	158·1	205·4	287·1
43·7	1·0665	102·4	121·0	144·5	166·5	216·9	302·8
80	1·0375	107·4	127·2	151·6	174·9	227·8	317·6
99·2	1·0220	109·4	129·7	154·5	178·3	226·6	324·2

Nicotine in α-bromonaphthalene. Some naphthalene was also present as impurity. No rotations could be observed at 0° owing to partial solidification of the mixture, $p = 4{\cdot}3213$. Densities determined: 1·4668 at 10·7°; 1·4335 at 45·2°; 1·4081 at 70·4°; 1·3788 at 100°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
12·6°	1·4650	−111·4°	−133·6°	−163·5°	−188·9°	−241·2°	−337·9°
41·1	1·4367	117·1	139·0	166·7	191·4	244·7	342·3
69·6	1·4085	119·9	140·3	168·1	192·6	252·2	345·9
99·2	1·3800	121·1	141·0	167·4	194·5	254·1	343·8

Homogeneous nicotine. Densities determined: 1·0124 at 14·8°; 0·99037 at 41·0°; 0·9688 at 70°; 0·9449 at 99·2°.

t.	*d.*	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_v$.
0°	1·0212	−175·6°	−202·8°	−371·2°
14·2	1·0108	176·4	204·2	372·8
39	0·9925	177·9	206·0	376·1
71·5	0·9673	179·3	207·1	377·0
99	0·9453	179·7	207·2	377·1

Nicotine in ethyl acetate. The rotation values for the highest temperature show a sudden rise in the absolute sense; this may be due in part to loss of solvent at that temperature, $p = 10{\cdot}701$. Densities determined: 0·9143 at 15°; 0·8893 at 37·7°; 0·8569 at 64·7°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	0·9294	−127·7°	−151·0°	−180·7°	−208·2°	−268·8°	−376·8°
15·2	0·9135	129·0	152·1	181·0	209·4	269·1	378·2
40·8	0·8855	127·0	153·7	182·6	210·5	274·0	380·9
60	0·8626	116·2	141·3	171·0	198·1	253·2	355·9

Nicotine in water, $p = 9{\cdot}3930$. Densities determined: 1·0060 at 15·1°; 1·0003 at 32·8°; 0·9912 at 52·6°; 0·9820 at 68·5°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·0098	−54·57°	−64·68°	−77·15°	−90·25°	−119·0°	−170·0°
24·5	1·0031	58·74	70·15	83·41	97·22	127·5	182·4
47·5	0·9935	63·07	75·40	89·69	104·4	137·3	194·7
67·6	0·9827	68·08	80·18	95·63	111·1	144·7	205·4

Nicotine in excess of sulphuric acid. To 3·5241 g. of nicotine were added 24 c.c. of 3·2095*N*-H_2SO_4, $p = 11{\cdot}880$. Densities determined: 1·1085 at 13·8°; 1·0920 at 46·8°; 1·0798 at 67°; 1·0645 at 90°.

t.	*d.*	$[\alpha]_{r_1}$.	$[\alpha]_{r_2}$.	$[\alpha]_y$.	$[\alpha]_g$.	$[\alpha]_b$.	$[\alpha]_v$.
0°	1·1145	+22·10°	+25·63°	+30·30°	+34·46°	+43·43°	+58·06°
26·6	1·1027	18·46	21·56	25·48	29·39	37·45	49·61
44·8	1·0931	16·41	19·30	22·86	26·23	33·06	44·56
66·8	1·0800	14·37	16·76	20·02	22·70	28·74	38·58
90	1·0645	12·16	14·33	17·05	19·42	24·56	32·86

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UNIVERSITY OF GLASGOW. [*Received, July 6th,* 1925.]

CCCXXXII.—p-*Dimethylaminodiphenylacetic Acid.*

By Dalip Singh.

Vorländer and Siebert have shown (*Ber.*, 1906, **39**, 1024) that barium diphenylacetate on distillation gives, together with other products, tetraphenylallene. The preparation of p-*dimethylaminodiphenylacetic acid* (III) was therefore undertaken, for should its barium salt (I) decompose in like manner, the product, tetramethyldiaminotetraphenylallene (II), would furnish a suitable material for testing van 't Hoff's view of the molecular asymmetry of compounds of the substituted allene type.

$$\underset{\text{(I.)}}{\left(\begin{matrix}NMe_2\cdot C_6H_4\\ Ph\end{matrix}\!>\!CH\cdot CO_2\right)_2}Ba \longrightarrow \underset{\text{(II.)}}{\begin{matrix}NMe_2\cdot C_6H_4\\ Ph\end{matrix}\!>\!C{:}C{:}C\!<\!\begin{matrix}C_6H_4\cdot NMe_2\\ Ph\end{matrix}}$$

The desired synthesis was effected by hydrolysing *ethyl* p-*dimethylaminobenzilate* (V), prepared by the action of *p*-dimethylaminophenylglyoxylic ester (IV) (Guyot, *Compt. rend.*, 1907, **144**, 1120) on magnesium phenyl bromide, to the corresponding *acid* (VI) and reducing the latter with hydriodic acid and phosphorus.

$$\underset{\text{(IV.)}}{NMe_2\cdot C_6H_4\cdot CO\cdot CO_2Et} \longrightarrow \underset{\text{(V.)}}{NMe_2\cdot C_6H_4\cdot CPh(OH)\cdot CO_2Et} \longrightarrow \underset{\text{(VI.)}}{NMe_2\cdot C_6H_4\cdot CPh(OH)\cdot CO_2H} \longrightarrow \underset{\text{(III.)}}{NMe_2\cdot C_6H_4\cdot CHPh\cdot CO_2H}$$

Difficulties, eventually overcome, were encountered in the Grignard reaction. The reagent readily attacked the dimethylamino-group and the whole of the ester was precipitated in the form of a compound. (This, on decomposition with water, regenerated the original ester and therefore probably had the constitution $MgPh\cdot NMe_2Br\cdot C_6H_4\cdot CO\cdot CO_2Et$; compare Kauffmann, *Ber.*, 1913, **46**, 2929.) Moreover, the use of too great an excess of the Grignard reagent had to be avoided, otherwise the carbethoxy-group of the ester also was attacked and the *glycol*

$$NMe_2\cdot C_6H_4\cdot CPh(OH)\cdot CPh_2\cdot OH \text{ (VII)}$$

produced.

The best results in the desired direction were achieved by adding an ethereal solution of the ester (IV) to the Grignard reagent (2·5 mols.) and working up the product immediately.

The behaviour of barium, calcium, and lead *p*-dimethylaminodiphenylacetates on dry distillation was investigated. The dry salt was distilled in a high vacuum in a specially designed apparatus. From the barium salt an oil was obtained, from which a crystalline solid, having the composition of *di*-p-*dimethylaminobenzhydryl ketone*, $CO(CHPh\cdot C_6H_4\cdot NMe_2)_2$ (VIII), and *p*-dimethylaminodiphenylmethane were isolated, but none of the allene derivative (III). Now, although Vorländer and Siebert obtained a considerable

quantity of diphenylmethane together with tetraphenylallene by distilling barium diphenylacetate, they were unable to detect any dibenzhydryl ketone. It would appear, therefore, that the presence of the tertiary amino-group in dimethylaminodiphenylacetic acid favours the formation of the ketone and prevents that of the allene.

The preparation of *ethyl phenyl*-4-*pyridylpyruvate*,

$$C_5NH_4{\cdot}CHPh{\cdot}CO{\cdot}CO_2Et \text{ (IX)},$$

was next undertaken. This compound is a possible source of phenylpyridylacetic acid, from which a substituted allene of the desired type might be obtained. The ester was synthesised by condensing 4-benzylpyridine and ethyl oxalate with potassium ethoxide (compare Wislicenus, *Ber.*, 1909, **42**, 1140). The acid produced by hydrolysing the ester was unstable and difficult to purify. Its sodium salt was oxidised by hydrogen peroxide with formation of sodium phenylpyridylacetate. The acid liberated from this immediately decomposed into benzylpyridine and carbon dioxide.

Corresponding condensations of benzylpyridine with other esters such as ethyl benzoate, ethyl formate, and ethyl carbonate could not be carried out.

Experimental.

Ethyl p-*Dimethylaminobenzilate* (V).—To a well-cooled ethereal solution of the Grignard reagent prepared from magnesium (3 g.) and bromobenzene (19·5 g.) is gradually added an ethereal solution of ethyl *p*-dimethylaminophenylglyoxylate (11 g.), and the reaction mixture is immediately poured on to a mixture of ice and dilute hydrochloric acid. The aqueous layer is treated with ammonium chloride and ammonia and extracted with ether. From the washed extract, dried with potassium carbonate, an oil is obtained which changes to a pasty solid on scratching; this is filtered off and crystallised from absolute alcohol. The *ester* thus obtained (yield 9 g.) melts at 96—97° (Found: C, 72·1; H, 7·1; N, 4·5. $C_{18}H_{21}O_3N$ requires C, 72·2; H, 7·0; N, 4·7%). It is very soluble in chloroform, benzene, or acetone, less soluble in ethyl or methyl alcohol, or ether, sparingly soluble in petroleum, and insoluble in water.

p-*Dimethylaminotetraphenylethylene glycol* (VII) is obtained as a by-product of the preceding reaction when too great an excess of the Grignard reagent has been used. The yield increases considerably if the reaction mixture is kept for a long time before being decomposed; and on heating, the *glycol* is almost the sole product. It is worked up in the same manner as the hydroxy ester. It separates from much boiling alcohol in glistening crystals m. p. 193—194° (Found: C, 82·2; H, 6·4; N, 3·3. $C_{28}H_{27}O_2N$ requires C, 82·1; H, 6·6; N, 3·4%), which are soluble in benzene

acetone, chloroform or acetic acid, and sparingly soluble in ethyl or methyl alcohol, or ether.

p-*Dimethylaminobenzilic Acid* (VI).—The ester (V) is heated under reflux with a slight excess of alcoholic sodium hydroxide for 4 hours, the alcohol evaporated, and the alkaline solution, after being shaken with ether to remove unchanged material, exactly neutralised with dilute sulphuric acid. The *acid*, isolated by means of ether, is obtained as a crystalline solid, m. p. 50—55°, after drying in a vacuum desiccator (Found : C, 69·5; H, 6·5. $C_{16}H_{17}O_3N$ requires C, 70·8; H, 6·3%). It is unstable, becoming yellow and finally green on keeping, and yellow on warming. It is very soluble in most of the organic solvents, except light petroleum, but is recovered from the solutions in a viscous condition.

p-*Dimethylaminodiphenylacetic Acid* (III).—The sodium salt of the hydroxy-acid (10 g.; obtained by evaporating an alkaline solution prepared as described above) is gently boiled under reflux with red phosphorus (5 g.) and constant-boiling hydriodic acid (50 c.c.) for about 6 hours. The diluted, filtered solution deposits, on cooling, colourless crystals of the hydriodide of *p*-dimethylaminodiphenylacetic acid. This, after being washed with a little water, is exactly neutralised, in aqueous solution, with ammonia, methyl-orange being used as indicator. The *acid* is then extracted with ether, and crystallised from hot alcohol, separating in silky, white needles, m. p. 104—105° (Found : C, 75·5; H, 6·8; N, 5·3. $C_{16}H_{17}O_2N$ requires C, 75·3; H, 6·7; N, 5·5%). It dissolves readily in chloroform, acetone, or benzene, less readily in ethyl or methyl alcohol or ether, and is sparingly soluble in light petroleum.

Di-p-*dimethylaminobenzhydryl Ketone* (VIII).—In a glass tube, sealed at one end and provided with an air-tight glass stopper at the other, is placed a cylindrical copper vessel filled with 2 g. of barium *p*-dimethylaminodiphenylacetate, thoroughly dried at 150—160°. The tube is connected by means of a side tube with a charcoal–liquid air vacuum apparatus, which can communicate by a three-way tap with a Fleuss pump or with the atmosphere. The whole apparatus is evacuated first with the pump and then by means of the charcoal cooled in liquid air. Heating is effected by a metal bath, and the distillation is continued so long as reddish-brown oil collects in a bulb blown in the tube near its sealed end.

The oil is washed with acetone. The washings slowly deposit a white solid, which crystallises from much boiling alcohol in thin needles, m. p. 190° (Found : C, 83·5, 83·3; H, 7·2, 7·1. $C_{31}H_{32}ON_2$ requires C, 83·0; H, 7·1%). The *ketone* dissolves readily in chloroform or carbon disulphide, is fairly easily soluble in ether or petroleum, less soluble in benzene or acetone, and very sparingly soluble in

ethyl or methyl alcohol. Its behaviour towards ketonic reagents was not examined, as the less complex dibenzhydryl ketone was known to be inert towards hydroxylamine, phenylhydrazine, and semicarbazide (Vorländer and Rack, *Ber.*, 1923, **56**, 1126).

The oil remaining after the ketone has been removed is fractionally distilled; the greenish-brown oil that passes over at 175°/2—3 mm. solidifies when cooled and scratched. By crystallising it from petroleum, *p*-dimethylaminodiphenylmethane (Limpricht, *Annalen*, 1899, **307**, 310) is obtained in thin leaflets, m. p. 31° (Found: C, 85·6; H, 8·0. Calc., C, 85·3; H, 8·0%).

Ethyl Phenyl-4-pyridylpyruvate (IX).—To a solution of potassium ethoxide (1 g. potassium) in 4 g. of alcohol are added in turn ether (20—30 c.c.), ethyl oxalate (3·8 g.), and 4-benzylpyridine (4·3 g.; 1 mol.). After 12 hours, the yellow potassium salt that has been deposited is decomposed by a slight excess of glacial acetic acid, ice-water added, and the ester together with the uncondensed material extracted with ether. From the washed and dried extract a solid is obtained which separates from alcohol in glistening, yellow crystals, melting at 123—124° to a yellowish-green liquid (yield about 33%) (Found: C, 71·3; H, 5·7; N, 5·4. $C_{16}H_{15}O_3N$ requires C, 71·4; H, 5·6; N, 5·2%). The *ester* is fairly easily soluble in benzene, chloroform, or acetone, less soluble in ethyl or methyl alcohol, sparingly soluble in ether, and insoluble in light petroleum.

The ester is left over-night in a cold dilute alcoholic solution of sodium hydroxide, water is then added, and the unchanged material removed with ether. The alkaline solution is acidified with acetic acid and shaken with chloroform. The chloroform in the extract is evaporated in a current of air, and the residue is freed from acetic acid by soda–lime in a desiccator. *Phenyl-4-pyridylpyruvic acid* is thus obtained as a yellow oil which solidifies when rubbed with benzene or crystallised from alcohol. It turns green at 100° and melts indefinitely at 110° (Found: C, 72·7; H, 5·2; N, 6·1 $C_{14}H_{11}O_3N$ requires C, 69·7; H, 4·6; N, 5·8%). The acid is very soluble in alcohol, acetic acid, or acetone, less soluble in benzene, and very sparingly soluble in light petroleum.

Phenylpyridylpyruvic acid oxime hydrochloride is obtained by mixing equivalent quantities of hydroxylamine hydrochloride and sodium phenylpyridylpyruvate in aqueous solution; crystals m. p. 52—53°, of the *hydrochloride* are deposited after 12 hours (Found: C, 57·4; H, 4·3. $C_{14}H_{12}O_3N_2$,HCl requires C, 57·4 H, 4·4%).

Sodium Phenyl-4-pyridylacetate.—On addition of the calculated quantity of hydrogen peroxide (30%) to an aqueous solution

sodium phenylpyridylpyruvate, there is a rapid evolution of gas; the colour is completely discharged in about 1 hour. The solution of the sodium salt thus obtained, on being acidified, gives some 4-benzylpyridine, which is probably produced by decomposition of phenylpyridylacetic acid.

2-α-4-*Pyridylbenzyl*-3-*quinoxalone*, $C_6H_4<\begin{matrix}N=C\cdot CHPh\cdot C_5NH_4\\ NH\cdot CO\end{matrix}$.—Alcoholic solutions of equimolecular quantities of ethyl phenyl-4-pyridylpyruvate and *o*-phenylenediamine are heated together on a water-bath for 2 hours; the solid that separates is washed, and crystallised from hot pyridine; m. p. 294—295° (Found: C, 76·7; H, 4·8; N, 13·0. $C_{20}H_{15}ON_3$ requires C, 76·7; H, 4·8; N, 13·4%).

This work was carried out under the supervision of Dr. W. H. Mills, F.R.S., and the author is indebted to Prof. Sir William Pope for providing facilities in the laboratory.

University Chemical Laboratory,
Cambridge. [*Received, July 30th,* 1925.]

NOTES.

Selenium as a Chlorine Carrier. By Oswald Silberrad and Charles A. Silberrad.

The observations (Silberrad, C. A. Silberrad, and Parke, this vol., p. 1724) that selenium acted as a catalyst towards sulphuryl chloride in a perfectly normal manner, *i.e.*, midway between tellurium and sulphur, and that the catalysts examined appeared to behave as chlorine carriers rather than as dissociation catalysts made it of interest to reinvestigate Willgerodt's work (*J. pr. Chem.*, 1885, **31**, 539; 1888, **34**, 264) on direct chlorination, which led him to the conclusion that selenium does not act, in that case, as a chlorine carrier at all.

To this end dual experiments were conducted. Chlorine (1 mol.) was passed into boiling toluene (1) without and (2) with the addition of selenium chloride; each experiment was repeated (*a*) in total darkness and (*b*) in an apparatus so arranged that the vapour was exposed to light; the quantities of chlorotoluene and benzyl chloride produced were determined as recently described (*loc. cit.*). The results were as follows:

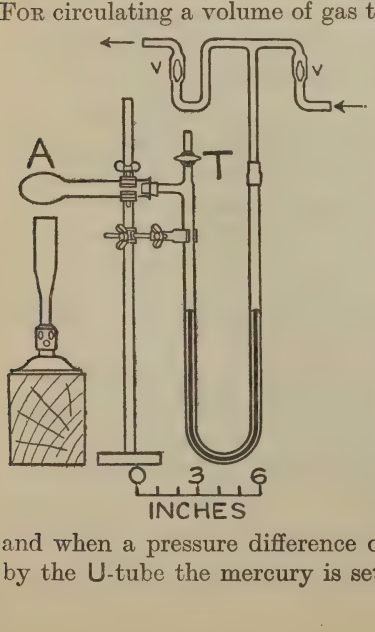
Conditions of expt.	$d_4^{16°}$.	Composition of product %. Chlorine.	Toluene.	Chlorotoluene.	Benzyl chloride.	Ratio Chlorotoluene/benzyl chloride.
(*a*) In total darkness.						
No catalyst	0·961	12·4	55·8	2·7	41·5	0·065
With selenium (1·0 g. of $SeCl_4$)*	0·983	15·8	43·4	33·7	22·9	1·472
(*b*) Vapour exposed to light.						
No catalyst	0·988	16·2	42·3	10·6	47·1	0·225
With selenium (0·3 g. of $SeCl_4$)*	1·004	18·3	34·6	29·5	35·9	0·82

* The selenium chloride was prepared by passing dry chlorine over the element, with which, contrary to the literature (Sacc, *Ann. Chim. Phys.*, 1848, **23**, 124), both varieties react at the ordinary temperature, passing through the mono- to the tetra-chloride.

From these results it is evident that, contrary to the literature, selenium does act as a carrier in direct chlorination; its presence not only raises the ratio of nuclear to side-chain substitution, but also, to a lesser extent, increases the amount of chlorine which enters into combination in a given time.—The Silberrad Research Laboratories, Buckhurst Hill, Essex. [*Received, August* 11*th*, 1925.]

A Simple Form of Gas Circulating Apparatus. By A. R. Pearson and J. S. G. Thomas.

For circulating a volume of gas through a closed system, apparatus depending on the force-pump principle has been described by Bone and Sarjant (*Proc. Roy. Soc.*, 1919, **96**, *A*, 126) and by Davis, Place, and Edeburn (*Fuel*, 1925, **4**, 290); in each case the piston is mercury contained in a U-tube.



A prime mover for the mercury–U-tube type of circulating pump can be made very simply from ordinary laboratory apparatus, utilising the principle of the hot-air engine (see Griffiths, "The Thermal Measurement of Energy," 1901, p. 50). The complete apparatus is shown in the figure. The bulb A is heated by a burner, and when a pressure difference of two or three inches is indicated by the U-tube the mercury is set in oscillation by quickly opening

and closing the tap, T, in such a way that the pressure in the hot bulb is suddenly reduced as nearly as possible to equality with that on the other side of the U-tube. The mercury will then continue to oscillate as long as heat is supplied to the bulb, and by the operation of the glass valves, V, or other suitable valves, gas can be forced through the system in the direction of the arrows. To ensure regularity of operation, suitable dimensions must be chosen for the mercury column and the hot bulb. With the dimensions shown, the apparatus drives about 2 cubic feet of gas per hour against a total back pressure of about 3 inches of water.—SOUTH METROPOLITAN GAS CO., LONDON, S.E. 15. [*Received, July 15th*, 1925.]

The Action of Metals on Dipentene Dihydrohalide. Preparation of a Synthetic Diterpene. By KENNETH CHARLES ROBERTS.

ALCOHOLIC solutions of *cis*- and *trans*-dipentene dihydrobromide and of *trans*-dipentene dihydrochloride were each shaken at room temperature with molecular silver until reaction was complete, this being indicated when no precipitate was formed on dilution of a portion of the reaction mixture with water. The action of finely-divided copper was tried in the same way. (The action of sodium was investigated by Montgolfier, *Ann. Chim. Phys.*, 1880, **19**, 155). In no case was metal halide formed. There was therefore no condensation, but simply loss of halogen acid and production of dipentene. This polymerised to a diterpene, which was isolated as a colourless, highly viscous liquid with a faint terpene-like odour, b. p. 173—183°/13 mm., $n_D^{20°}$ 1·5170, $d^{20°}$ 0·9361 (Found: C, 88·4; H, 12·0; *M*, 273, 266; iodine value, 103. $C_{20}H_{32}$ requires C, 88·2; H, 11·8%; *M*, 272; iodine value, for one double linking, 94). β-Camphorene has b. p. 170—180°/10 mm., n_D 1·5180, and $d^{20°}$ 0·9300 (Semmler and Rosenberg, *Ber.*, 1913, **46**, 768).—UNIVERSITY OF OTAGO, NEW ZEALAND. [*Received, August 11th*, 1925.]

CCCXXXIII. — *Negative Adsorption. The Surface Tensions and Activities of Some Aqueous Salt Solutions.*

By ARTHUR KENNETH GOARD.

IN previous communications (Goard and Rideal, this vol., pp. 780, 1668) experiments were described dealing with the surface tensions of aqueous solutions of phenol containing sodium chloride, and the advantage of applying the Gibbs adsorption equation in its strict form, employing activities of the solute instead of its concentration,

was pointed out. Another case in which such a procedure is likely to prove fruitful is that of aqueous solutions of inorganic salts, which raise the surface tension of the solvent, being consequently negatively adsorbed at the surface of the solution. Little or no attempt seems to have been made hitherto to determine the magnitude of this negative adsorption. Langmuir (*J. Amer. Chem. Soc.*, 1917, **39**, 1848) has discussed the subject briefly, from the point of view of the orientation theory of surface tension. He considers that the surface of an aqueous salt solution probably consists of a single layer of oriented water molecules, and, from a few data on the surface tensions of potassium chloride solutions, concludes that the length of such an oriented water molecule is about 4 Å.U. He adds further that though different salts raise the surface tension of water to different extents, " these differences seem to be almost wholly accounted for by differences in the degree of electrolytic dissociation."

The data upon which Langmuir based this generalisation are somewhat scanty; and it seemed desirable to investigate this matter more fully, using wide ranges of concentration in order to determine whether the thickness of the adsorbed layer is independent of the concentration, and of the nature of the salt, as would seem to be necessary on Langmuir's view.

The salts chosen for this purpose were the chlorides of lithium, sodium, and potassium, cadmium chloride, and silver nitrate. For the first three salts, activity data are available up to the most concentrated solutions (compare Harned, *ibid.*, 1922, **44**, 252). The activity coefficient of cadmium chloride has been calculated by Lewis (G. N. Lewis and Randall, " Thermodynamics," New York, 1923) from the electromotive force measurements of Horsch (*J. Amer. Chem. Soc.*, 1919, **41**, 1787). This salt is unusual, in that the activity coefficient falls extremely rapidly as the concentration increases, dropping to 0·219 at a molarity of 0·0995 and to 0·025 at a molarity of 6·62. Commenting on this, Lewis remarks : " Cadmium chloride cannot be regarded as a strong electrolyte. It possesses in a lesser degree the characteristics of the analogous substance, mercuric chloride, which shows almost no ionisation." Unfortunately, no data are recorded for the activities of solutions between the two concentrations given above. Owing, however, to the comparatively small change of activity of the salt, it is possible to obtain fairly accurate values by means of graphical interpolation (assuming, of course, that the activity coefficient decreases continuously over this interval). Finally, provisional values for the activity coefficient of silver nitrate are given by Lewis, calculated from freezing-point measurements, and uncor-

rected for heat of dilution. They cannot therefore be regarded as strictly accurate save near the freezing point.

The surface tensions of the solutions were determined by the drop-weight apparatus previously described (Goard and Rideal, *loc. cit.*). Pure specimens of all the salts were obtained, except of lithium chloride, which gave a slightly alkaline solution. With this salt, therefore, the aqueous solution, after filtering, was evaporated to dryness and gently baked, the residue being subsequently dissolved in water and a little hydrochloric acid, and the salt recrystallised.

The solutions were kept over-night in a long vertical tube; a few c.c. were then run out from the lower end of the tube, and the supply bottle of the apparatus was subsequently filled. The apparatus was cleaned with hot chromic acid every time a fresh solution was employed.

The drop weights given in Table I are the means of several determinations, agreeing within 0·1%. The densities of the solutions were taken from Landolt's tables. All measurements were

TABLE I.

The Surface Tensions (σ) of Aqueous Salt Solutions at 20°.

Moles of salt per litre.	Mean wt. (g.) of ten drops.	Density.	σ (dynes/cm.).
	Lithium chloride.		
1·08	0·9353	1·024	74·74
1·94	0·9538	1·044	76·22
3·51	0·9931	1·078	79·46
	Sodium chloride.		
1·00	0·9343	1·036	74·78
2·00	0·9544	1·077	76·51
3·22	0·9819	1·110	78·73
5·00	1·0277	1·118	82·20
	Potassium chloride.		
1·00	0·9316	1·044	74·55
2·00	0·9503	1·088	76·13
3·00	0·9681	1·129	77·77
3·80	0·9832	1·182	79·17
	Cadmium chloride.		
0·471	0·9237	1·068	74·04
0·942	0·9303	1·136	74·67
2·36	0·9554	1·344	76·80
3·49	0·9823	1·543	79·20
4·71	1·0108	1·672	82·10
	Silver nitrate.		
1·00	0·9257	1·118	74·37
2·00	0·9360	1·236	75·23
3·00	0·9437	1·348	75·94
5·00	0·9721	1·402	77·69

made at 20°. The salt content of the solutions was checked by titration. The surface tensions were calculated by Iredale's method (see Goard and Rideal, *loc. cit.*).

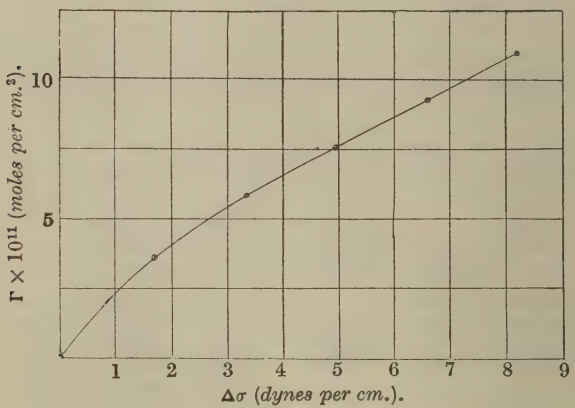
The form of the surface tension–concentration curves obtained from these figures is similar, in the case of the three alkali chlorides, to that described by previous observers (compare a collection of data made in 1920 by Stocker, *Z. physikal. Chem.*, **94**, 149), *i.e.*, the curves exhibit throughout a slight convexity towards the

concentration axis. With cadmium chloride and silver nitrate, however, the curves are initially *concave* towards this axis, up to a point of inflexion, which occurs with the former salt at a concentration of 2·2 molar, and with the latter at about 2·5 molar. Beyond these points, the curves are convex to the concentration axis. These would seem to be the only cases of such a relationship which have so far been observed. With silver nitrate, neither portion of the curve exhibits such pronounced curvature as obtains with cadmium chloride; the point of inflexion is nevertheless unmistakable.

Determination of the Surface Adsorption.

The negative adsorption, Γ, at the surface of these solutions was determined by plotting the surface tension against the logarithm

FIG. 1.



of the activity of the salt; Γ, which is proportional to the slope of this curve, was measured by drawing tangents. The activity coefficients of the first four salts in Table I were measured at 25°; the change in the coefficient over five degrees of temperature, however, may be considered to be negligible.

Owing to the approximation to a linear relation between surface tension and concentration, it was possible to read off with considerable accuracy values of the surface tension intermediate between those given in the above table. Since, however, the logarithm of the activity tends to an infinite negative value as the concentration approaches zero, direct determination of the slope of the surface tension–log. activity curve became inexact at low concentrations. It was found that if Γ were plotted against the elevation of the surface tension, a smooth curve was obtained which could be extrapolated back to low concentrations with fair accuracy.

On the " kinetic " view of surface films, such a procedure is analogous to plotting the reciprocal of volume against pressure (compare Langmuir, *loc. cit.*).

The results obtained with sodium chloride are shown in Fig. 1. Similar results were obtained with the other alkali chlorides.

In Table II, values of the negative adsorption, Γ, are given together with the corresponding *molarities* (moles of salt per 1000 g. of water). In the third column are given values of the thickness of the adsorption layer, calculated from the equation $\tau = 1000\Gamma/M$, where M = the salt concentration in moles/litre. Some discussion of the meaning of τ is given in the sequel.

Fig. 2 shows the values of τ plotted against the molarity of salt, for solutions of the three alkali chlorides.

Table II.

Adsorption at the Surface of Aqueous Salt Solutions.

Molarity.	$\Gamma \times 10^{11}$ (moles/cm.²).	τ (Å.U.).	Molarity.	$\Gamma \times 10^{11}$ (moles/cm.²).	τ (Å.U.).	Molarity.	$\Gamma \times 10^{11}$ (moles/cm.²).	τ (Å.U.).
Lithium chloride.			*Sodium chloride.*			*Potassium chloride.*		
0·1	0·55	5·5	0·1	0·60	6·0	0·1	0·40	4·0
0·2	1·05	5·25	0·2	1·15	5·75	0·2	0·83	4·2
0·5	2·10	4·25	0·5	2·30	4·7	0·5	2·15	4·4
1·0	3·19	3·2	1·0	3·65	3·75	1·0	3·75	3·85
2·0	4·63	2·3	2·0	5·9	3·05	2·0	6·10	3·25
3·0	5·90	2·1	3·0	7·6	2·7	3·0	8·05	2·95
			4·0	9·35	2·55	4·0	9·8	2·75
			5·0	11·0	2·45			

The results obtained with cadmium chloride are extremely interesting. Fig. 3 shows the adsorption coefficient plotted against the rise of surface tension. The curve exhibits two well-marked points of inflexion, and its earlier and later portions are coincident with two curves of the type shown in Fig. 1; these curves are dotted in the diagram and labelled I and II respectively.

Table III.

Cadmium Chloride Solutions.

Molarity.	$\Gamma \times 10^{11}$ (moles/cm.²).	τ actual (Å.U.).	τ_{I}.	τ_{II}.	Molarity.	$\Gamma \times 10^{11}$ (moles/cm.²).	τ actual (Å.U.).	τ_{I}.	τ_{II}.
0·05	0·34	6·8	6·8	—	2·0	9·1	4·9	2·2	5·3
0·1	0·60	6·0	6·0	—	3·0	13·8	5·1	—	5·2
0·2	1·04	5·2	5·2	—	4·0	17·6	5·1	—	5·2
0·3	1·46	4·9	4·9	—	5·0	21·2	5·1	—	5·1
0·5	2·08	4·25	4·2	7·4	6·62	26·1	5·0	—	5·0
1·0	3·74	3·9	3·1	6·0					

The values of τ, of course, exhibit the same anomalies. In Table III, column 3 gives the actual values of τ; column 4 gives the values of τ derived from curve I of Fig. 3, column 5 the values derived from curve II. If these be plotted against molarity, it will be seen that the actual τ curve is coincident in its earlier and later portions with two curves of the type exhibited by sodium chloride in Fig. 2.

The results obtained with silver nitrate are in some respects similar to those given by cadmium chloride. Values of Γ, plotted against the elevation of the surface tension, lie on a curve of normal type up to a molarity of 2; beyond this point, they increase at an abnormal rate, as do those of cadmium chloride. In this case, however, the increase is so great that it indicates that the activity

FIG. 2.

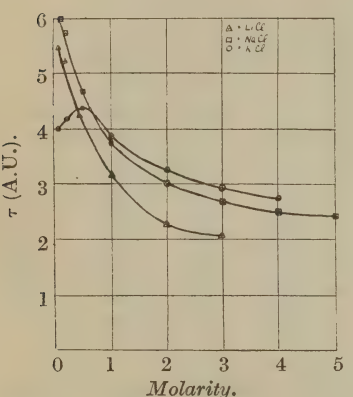
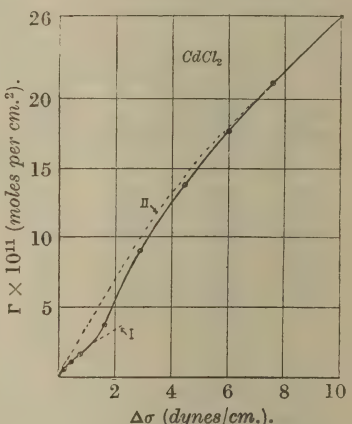


FIG. 3.



data are inaccurate at high concentrations. This was to be expected, in view of the fact that they are uncorrected for heat of dilution. Nevertheless, seeing that the form of the surface tension–concentration curve resembles that given by cadmium chloride (*vide supra*), it is probable that the abnormal increase of Γ at high concentrations is to some extent real, though exaggerated by the inaccurate activity values.

TABLE IV.

Silver Nitrate Solutions.

Molarity.	$\Gamma \times 10^{11}$ (moles/cm.²).	τ (Å.U.).	Molarity.	$\Gamma \times 10^{11}$ (moles/cm.²).	τ (Å.U.).
0·1	0·55	5·5	2·0	5·4	2·8
0·2	1·15	5·75	3·0	8·0	2·8
0·5	2·4	4·9	4·0	(43)	(12)
1·0	3·9	4·0	5·0	Very high	Very high

Discussion of Results.

It is evident that the values which have been obtained for the adsorption coefficients, and for the thicknesses of the adsorbed layers, are not such as to lead to the conclusion that the surface layer of different salt solutions consists of a single layer of oriented water molecules, since the thickness, τ, is independent neither of the concentration nor of the nature of the salt. This thickness represents of course the distance of the solute boundary from the surface of the solution, assuming that the concentration gradient at the solute boundary is infinitely steep. Such calculation of τ does not discriminate between ions of opposite sign; assuming, however, that the distribution of the chlorine ions in the solutions of the three alkali chlorides is the same, it would appear that the lithium ion comes nearest to the surface, the order followed by the ions being that of their atomic radii. It is possible that the decrease in the values of τ as the concentration of the solution increases is due to the " water shells " with which the ions have been supposed to be surrounded (compare Born, *Z. Physik*, 1920, **1**, 221; also Lorenz, *Z. Elektrochem.*, 1920, **26**, 424) becoming smaller or more tightly packed.

Some experiments upon the nature of the negative adsorption layer have been recently made by Frumkin (*Z. physikal. Chem.*, 1924, **109**, 34), who, however, deals chiefly with anions. Values are given in his paper for the adsorption of the three alkali chlorides in $2N$-solution, which are in fair agreement with those given here.

In considering the phenomena exhibited by cadmium chloride solutions, it seems difficult to avoid the conclusion that we are dealing with two molecular species. Knowing cadmium chloride to be a weak electrolyte, we may be fairly confident in ascribing the earlier portion of the adsorption curve to the influence of ions, and the later portion to that of molecules.

The resemblance of the surface tension–concentration curve of silver nitrate to that of cadmium chloride also indicates the existence of molecules in concentrated solution, though the activity data are not sufficient to warrant a definite conclusion.

Summary.

The negative adsorption at the surface of aqueous solutions of lithium, sodium, potassium, and cadmium chlorides, and of silver nitrate, has been determined over wide ranges of concentration, employing original surface tension determinations, by the drop-weight method, and activity data from various sources. The results obtained are not in harmony with the supposition that the

surface of these solutions consists of a single layer of oriented water molecules, as has been supposed by Langmuir; since the mean thickness of the adsorbed layer varies with the concentration of the solution and with the nature of the salt.

Evidence is adduced which indicates that in concentrated solutions of cadmium chloride, and possibly of silver nitrate, the adsorption is determined by undissociated molecules, as well as by ions.

The author wishes to thank Dr. E. K. Rideal for the helpful interest he has taken in this work during its prosecution.

LABORATORY OF PHYSICAL CHEMISTRY,
CAMBRIDGE. [*Received, June 3rd,* 1925.]

CCCXXXIV.—*Polarity Theories and Four-membered Rings. The Non-existence of* 2 : 3 : 3-*Triphenylmethylene*-1 : 2-*oxaimine.*

By GEORGE NORMAN BURKHARDT, ARTHUR LAPWORTH, and JAMES WALKDEN.

INGOLD and WEAVER discussed the formation of a four-membered ring compound from phenylazocarboxylic ester and diphenylketen (this vol., p. 378) and added in a footnote: " The direction of this addition conforms to the theory of alternate polarities, unlike many of the cases previously discussed " (compare, for instance, Ingold and Weaver, J., 1924, **125**, 1456).

It has since been shown (this vol., pp. 1747, 2234) that in most of the cases there alluded to it is the experimental data and the interpretation thereof which were at fault and not the theory of alternate polarities. Only one case investigated by Ingold and his co-workers remained which offered any difficulties from the point of view of polarity theories, and this is now dealt with.

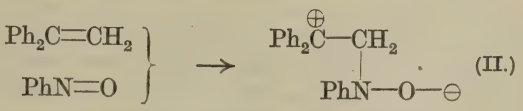
This last case concerns the action of nitrosobenzene on *as*-diphenylethylene. Ingold and Weaver (J., 1924, **125**, 1461) obtained a compound which in its stability towards permanganate and its general properties (except thermal division) closely resembled those of the " dimethyleneoxamines " described in the same paper. The compound was assigned the formula $CPh_2<^{CH_2}_{NPh}>O$ (I.) and its formation was held to constitute evidence against the theory of induced alternate polarities. In order to explain why the present authors remained sceptical of this formula, it will be simplest to deal with first principles, which tend to be overlooked in discussions of secondary details.

Lapworth suggested that many reactions in organic chemistry are due to formation and decomposition of complex ions (J., 1901, **79**, 1266). It is not a long step from this elementary conception to the idea that two molecules A and K, in one or both of which polarisation occurs, may unite with each other to form a bipolar ion $\oplus$A—K$\ominus$, provided that the residues $\oplus$A and K$\ominus$ have sufficiently high affinities for their respective charges.*

According to Robinson's theory of polarisation in nitrosobenzene, addition of an ion, whether charged negatively or positively, to the nitroso-group should normally take place at the nitrogen atom (*Chem. and Ind.*, 1925, **44**, 456).

Lapworth has deduced from the properties of ethenoid hydrocarbons (compare *ibid.*, p. 228) certain conclusions which can be expressed in the following terms : (*a*) such hydrocarbons normally form positively charged ionic residues, and (*b*) the positions at which they combine with other ions and molecules in forming such ionic residues are those corresponding with the reactive positions as required by Thiele's theory.

A combination of these theories leads to the view that the first step in the union of the nitroso-group of nitrosobenzene and the ethylenic carbon pair of *as*-diphenylethylene is the bipolar ion (II).



(II.)

Normally (II) would change into $CHPh_2{\cdot}CH{:}NPh{:}O$, the customary formula for a nitrone being employed.

The formula of the hypothetical first complex is given here in the simplest possible form, and recondite details such as those of possible preliminary activation of one or both of the two reacting molecules, partial *versus* whole valencies, conjugation phenomena within the complex bipolar ion, and the localisation or dispersion of the positive charge over the diphenylcarbonium system, $\overset{\frown}{Ph_2C}$—, must be omitted from this short statement.

It was evident, therefore, that if the compound obtained by Ingold and Weaver had the constitution which they ascribed to it, some entirely novel factor had caused the complete inversion of

* This is expressed in terms of the electro-affinity theory of Abegg and Bodländer. There are various alternative modes of expressing the idea : for example, " $\oplus$A and K$\ominus$ must represent residues of sufficient stability, in the sense of large entropy." Thus $\oplus$A has stability when it represents the residue of an ammonium ion.

Throughout the present paper the signs $\oplus$ and $\ominus$ are used to denote electrical *charges*, not latent polarities or key-atom signs.

the normal properties either of the nitroso-group or of the hydrocarbon molecule. Such a conclusion was one which could not be accepted without the most stringent proof.

The present authors therefore prepared the compound descr bed by Ingold and Weaver and observed in the first place that when in solution in weak methyl alcohol it was easily oxidised in the cold by ferric chloride, so that after subsequently diluting, extracting with ether, and evaporating the latter at the ordinary temperature, a marked odour of nitrosobenzene became perceptible. This rendered it highly improbable that an " oxaimine " ring was present.

It was next proved that the compound was totally different in properties from *N*-phenyl-*as*-diphenylacetaldoxime,

$$CHPh_2{\cdot}CH{:}NPh{:}O,$$

which was made in small quantity from *as*-diphenylacetaldehyde and *N*-phenylhydroxylamine, melted at a much lower temperature, and gave phenylcarbylamine when heated.

There remained only one conceivable explanation, namely, that the compound described by Ingold and Weaver had been formed as the result of a complex reaction in which a carbon atom had been lost, just as when styrene yields *N*-phenylbenzaldoxime (Ingold and Weaver, *loc. cit.*, p. 1462). This idea could not, of course, be reconciled with the statement that the compound on thermal division gave benzophenoneanil and formaldehyde (*loc. cit.*, p. 1461); but Ingold and Weaver did not specify the tests by which the formation of the latter was proved or the yield obtained. The compound when heated in an open test-tube certainly does give a pungent odour, but this is easily recognised as that of nitrosobenzene, evidently formed by a side reaction.

The analytical figures found by Ingold and Weaver are in even better agreement with the formula of *N*-phenyldiphenylnitrone, $CPh_2{:}NPh{:}O$, than with the formula (I) which they deduced. This nitrone had previously been made by Angeli, Alessandri, and Aiazzi-Mancini (*Atti R. Accad. Lincei*, 1911, **20**, i, 546) by the oxidation of β-phenyl-β-diphenylmethylhydroxylamine and later by Staudinger and Miescher (*Helv. Chim. Acta*, 1919, **2**, 568) by the action of nitrosobenzene on diphenyldiazomethane. The present authors prepared it by both methods, and found it to be identical in all respects with the compound described by Ingold and Weaver. The tests used were: mixed melting points, crystalline form, general qualitative behaviour towards solvents, production of nitrosobenzene by oxidation with ferric chloride in the cold as well as by heating in a test-tube.

It is clear, therefore, that nitrosobenzene acts upon *as*-diphenyl-

ethylene in very much the same way as it acts upon styrene and allied compounds, and in this connexion reference may be made to the work of Alessandri (*Gazzetta*, 1924, **54**, 426 *et seq.*).

Conclusion.—It has already been shown that there is no evidence of the formation of four-membered rings at any stage during the reaction of nitrosobenzene with (*a*) methylenemalonic ester (this vol., p. 1747) or (*b*) methylenearylamines (*ibid.*, p. 2234). The only remaining case investigated by Ingold and his co-workers and cited as an instance of four-membered ring formation proceeding in a direction contrary to the requirements of the theory of alternate polarities is the one dealt with in the present paper and here, as in the cases (*a*) and (*b*), such facts as have been fully established are in complete harmony with Robinson's theory of polar reactions of nitrosobenzene (*loc. cit.*) and in general with electrochemical conceptions of organic chemical reactions (compare Lapworth, *ibid.*, p. 228, and present paper).

THE UNIVERSITY, MANCHESTER. [*Received, July 28th*, 1925.]

CCCXXXV.—*The Distribution of Pyridine between Water and Benzene.*

By ROWLAND MARCUS WOODMAN and ALEXANDER STEVEN CORBET.

THE present paper deals with the distribution of pyridine between the two immiscible solvents water and benzene. The results given in the table and plotted on the triangular diagram show that the system water–pyridine–benzene constitutes an example of a pair of partly miscible liquids.

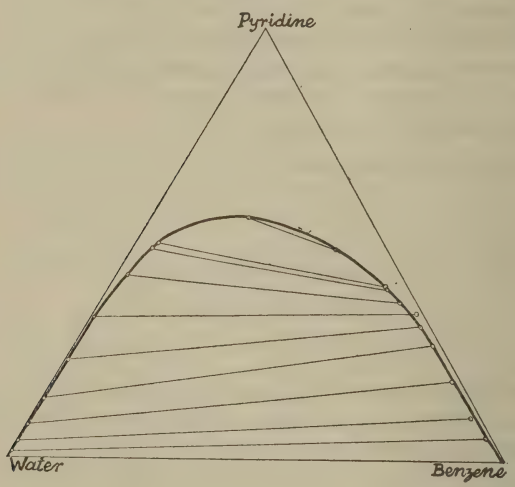
Over the range 0—6% of pyridine in the total system, the ratio of the weight percentages of this liquid in the benzene and water layers is about 2·7. This ratio then decreases with increasing concentration of pyridine, the system behaving, over a long range, in accordance with the system water–phenol–benzene (Rothmund and Wilsmore, *Z. physikal. Chem.*, 1902, **40**, 611; Philip and Clark, this vol., p. 1274). Then the ratio, after reaching a minimum of 0·8, rises again, finally to reach unity at the critical point.

This behaviour is unusual, and results in change of direction of the slope of the tie lines. It is in good agreement, however, with the densities obtained for the layers, for the curve showing densities of layers against pyridine content is very similar to the triangular composition curve, the density tie lines showing the same changes of slope, and the critical points on both diagrams corresponding.

Wright (*Proc. Roy. Soc.*, 1892, **50**, 372) gives triangle curves for

the system lead–tin–zinc which show the same changes of slope of tie lines, the curve at 650° especially behaving practically as that for the present system in this respect. He noticed that the upper tie lines converged together thus and regarded this as due to the formation of a definite compound of tin and zinc. A similar explanation of compound formation between solute liquid and one of the solvent liquids would possibly suffice for the present analogous system; it is worthy of note that the water layers, which were at first turbid, cleared with increasing concentration of pyridine, the benzene layers showing opposite behaviour.

FIG. 1.



EXPERIMENTAL.

The benzene was purified in the usual manner and boiled at 80·35—80·5°. The pyridine was "B.D.H. pure."

The densities of water, benzene, water saturated with benzene at 25°, and benzene saturated with water at 25° were all determined at 25°. The first and the third, and the second and the fourth, exhibited differences of a unit or so only in the third decimal place. For the purpose of the diagram, therefore, it could be assumed that no conjugate solutions were formed in the system benzene and water.

Measured volumes of benzene, water, and pyridine were placed in stoppered graduated cylinders. The mixtures were maintained at 25° in a thermostat for 6 hours, and were vigorously shaken periodically. After a final shaking, the stopper was removed from a cylinder and, after allowing a further 5 minutes in the thermostat, the volumes of the layers were noted.

Known volumes of the two layers were then pipetted into tared flasks, further weighings making possible calculation of the densities of the layers at 25°.

The pyridine was readily determined (in absence of ammonia or other bases) by titration with normal acid and methyl-orange (Allen's "Commercial Organic Analysis," 1912, VI, 138). When much benzene was present, water was added to the sample, and the course of the titration observed in the aqueous underlayer.

The estimation of the benzene (for which no accurate method could be found) was more difficult. Advantage was taken of the slight solubility of benzene in water. The pyridine present in a large sample having been neutralised, and a slight excess of acid added, the mixture was washed into a burette, and the volume of benzene noted, together with the temperature. A knowledge of the densities of benzene over the range 17—20° then allowed the calculation of weight percentages of the benzene in the layers. This procedure appeared satisfactory for the water layers, but experience showed that low results were sometimes obtained for the benzene layers. As in six out of the ten examples given the amount of benzene in the water layer was practically negligible, and as in three of the remaining cases it was less than 5%, it was quite justifiable to calculate the benzene in the benzene layer, knowing the total benzene used in the experiments, the volumes and densities of the layers formed, and the densities of benzene at different temperatures.

TABLE.

a is the ratio of pyridine % in the benzene layer to the pyridine % in the water layer. *b* is the ratio of grams of pyridine in 1 litre of the benzene layer to grams of pyridine in 1 litre of the water layer.

Benzene Layer.			Water Layer.				
Density.	% Py.	% C_6H_6.	Density.	% Py.	% C_6H_6.	*a*.	*b*.
0·874	3·28	94·54	0·994	1·17	0·0	2·803	2·465
0·882	9·75	87·46	0·995	3·55	0·0	2·746	2·438
0·893	18·35	79·49	0·998	7·39	trace	2·484	2·223
0·903	26·99	71·31	0·997	13·46	0·15	2·006	1·813
0·909	31·42	66·46	0·997	22·78	0·25	1·376	1·258
0·911	34·32	64·48	0·996	32·15	0·44	1·067	0·977
0·915	36·85	59·35	0·997	42·47	2·38	0·867	0·796
0·918	39·45	56·43	0·990	48·87	3·99	0·807	0·749
0·914	39·27	55·72	0·991	49·82	4·28	0·788	0·727
—*	48·39	40·85	0·972	56·05	19·56	0·863	—*

* Total benzene layer 4 c.c. only.

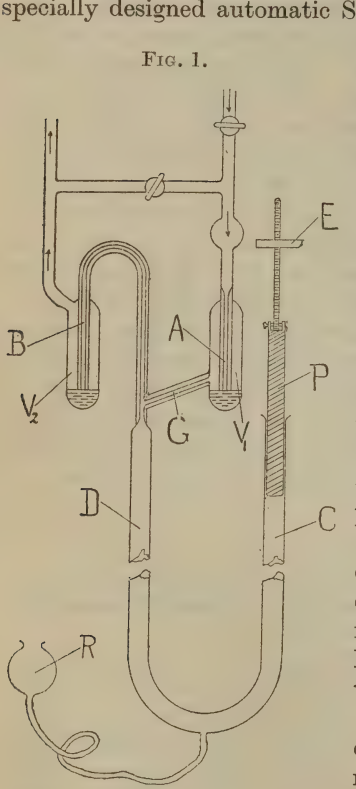
THE UNIVERSITY OF CAMBRIDGE. [*Received, July 17th*, 1925.]

CCCXXXVI.—*A Circulation Apparatus for Gases.*

By Nitya Gopal Chatterji and George Ingle Finch.

In the circulation apparatus used by Bone and his co-workers (J., 1902, **81**, 1903) in their numerous investigations of catalytic gas reactions, the gas is kept in steady circulation by means of a specially designed automatic Sprengel pump. This apparatus has been extensively used in gas research laboratories during the past 20 years, and for most purposes is quite satisfactory. It needs, however, considerable attention, and its rate of circulation is rather slow; thus, for example, when it is attached to an apparatus of about 1500 c.c. capacity the fastest possible rate is one circulation in about 20 minutes. And in order to ensure a steady rate of circulation, which is independent of any fluctuation of the water supply, the latter must be controlled by a subsidiary device. We have recently devised a new type of circulating pump for laboratory purposes, which Professor Bone considers is such a decided improvement upon his original design that he is adopting it in his laboratories, and it is at his suggestion that we are giving the following account of it.

Fig. 1.



The essential part of the apparatus consists of two small non-return mercury-sealed valves, which are alternately opened and closed by the periodic movement of a column of mercury. In the accompanying diagrammatic sketch of the apparatus, V_1 and V_2 are the two valves, into which are fused two capillary tubes, A and B. A side tube from V_2 and the capillary A are joined to either side of the main apparatus through which the circulation is to take place. The capillary B joined to the side tube from V_1 communicates with a long **U**-tube. A side tube at the lowest point of the bend of the **U**-tube is connected by means of rubber tubing to a mercury reservoir, R. The plunger, P, consisting of a wooden

rod, fitting loosely in C, is suspended from a cross-bar, E, rigidly fixed to a block of wood or metal sliding up and down between two vertical guides and driven by means of a crankshaft actuated by a geared-down motor. The U-tube is partially filled with mercury so that the downward movement of the plunger, P, displaces it in both arms of the U-tube. As the mercury rises in D, it compresses the gas above it, and the passage being blocked by the rise of mercury in the capillary A, the gas bubbles out through the mercury in valve V_2. On the other hand, when the plunger is withdrawn, the mercury descends in D, creating a partial vacuum above it, so that the gas is now sucked in through A, the capillary B being closed by the mercury in V_2. Thus during one complete movement of the mercury column in D the gas is once sucked in through A and forced out through B, maintaining the circulation of the gas in the direction of the arrows.

The circulation velocity of the gas depends in the main on the bore of the tube and the amplitude and rate of oscillation of the mercury column in it. In order to obtain the maximum velocity of circulation, the up and down motion of the plunger should synchronise with the natural period of oscillation of the mercury column in the U-tube. The length of the stroke of the mercury column can be altered either by raising or lowering the plunger, which is suspended from the cross-bar, E, by means of a length of 2BA threaded rod, or the mercury reservoir R.

In order that the apparatus may circulate efficiently, particularly at very low pressures, it is necessary to eliminate by the use of small bore tubing, as far as possible, all dead space above the column of mercury in D, without, however, impeding too much the flow of the gas. In valve V_1, the inner tube terminates about 1—2 mm. below the side tube, and the ends of the capillaries in both valves are cut and not rounded in a flame, whilst the quantity of mercury in the bulbs is just sufficient to cover the ends. Taps T_1 and T_2 enable the apparatus to be evacuated or filled with gas without the mercury in the valves splashing over. The valves may be filled with mercury *in situ ;* and whenever necessary, the mercury levels may be adjusted to optimum positions by suitably manipulating the reservoir R, with the taps T_1 and T_2 closed, when mercury may be added to or siphoned off from B until the end of the inner tube is just covered. Any mercury introduced into V_1 during this operation automatically overflows through G when the mercury level in the U-tube is lowered.

Several such circulation apparatus may be worked by a single motor, as a number of pistons may be attached to the same cross-piece. Three circulation apparatus of the type are at work in

these laboratories, two sets of four each and one of two. One of these has been in continuous work for more than 7 months, and the others for 4 months. With a U-tube bore of 1·5 cm., the maximum rate of circulation attained was 162 litres an hour. By adjusting the height of the plunger this could be cut down to a few c.c. per hour. With uniform movement of the plunger the rate of circulation is likewise uniform. The apparatus continues to circulate down to a pressure of 6 mm. of Hg. At a pressure of about 3 mm., circulation ceases.

The apparatus may be employed for the circulation of liquids. The mercury, since it is not agitated, and the circulating gases may be kept dry by phosphoric anhydride floating on the mercury in D and in the valves. This does not impede the smooth working of the apparatus.

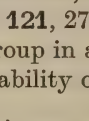
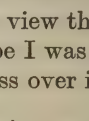
If static charges due to the friction between the mercury and the glass are removed by earthing the mercury contained in the valves and the U-tube, the mercury and the glass remain clean, and dust does not collect on the outside of the apparatus.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, July 21st,* 1925.]

CCCXXXVII.—*The Cyanine Dyes. Part IX. The Mechanism of the Condensations of Quinaldine Alkyliodides in Presence of Bases.*

By WILLIAM HOBSON MILLS and RICHARD RAPER.

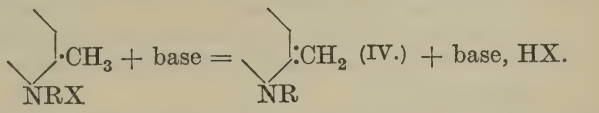
IN a discussion of the differences of reactivity shown by methyl groups adjacent to the nitrogen atom in heterocyclic bases of the quinoline, *iso*quinoline, and thiazole series one of us and J. L. B. Smith (J., 1922, **121**, 2724) were led to the view that the reactivity of the methyl group in a system of the type I was dependent upon the ability or inability of the system to pass over into the form II.

(I.)   (II.)

The reactivity of the methyl group on this view might be regarded as connected with the unsaturation of the nitrogen atom with which it was associated (compare Vorländer, *Ber.*, 1902, **35**, 4145). But it was also emphasised in that paper that the reactivity of such methyl groups is greater in the quaternary salts of the bases

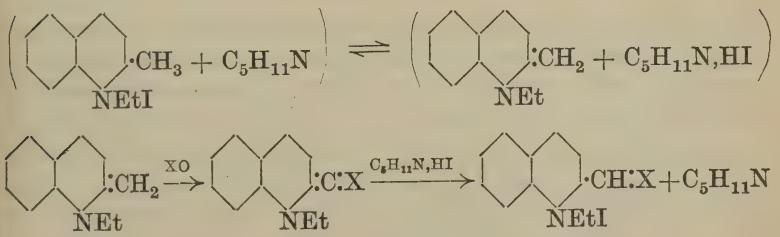
than in the bases themselves. The enhancement of the reactivity of the methyl group consequent on the addition of an alkyl group to the nitrogen atom called therefore for explanation, for this addition would be supposed to reduce the unsaturation to which the reactivity had been referred.

Since the condensations in question of the quaternary salts are brought about by the influence of strong bases, such as piperidine, the view was advocated that the actual substances through which the condensations were effected were the alkyl derivatives (IV) of the methylene bases (II) formed by the removal of the elements of the acid from the quaternary salts by the base used as condensing



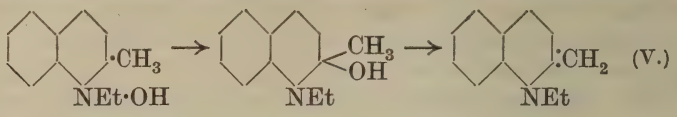
agent. The reactivity both of the bases and of their quaternary salts was thus referred to secondary products (II and IV) of the same type.

On this view, in a solution containing, for example, quinaldine ethiodide, piperidine and a substance of the type X:O, such as benzaldehyde or nitrosodimethylaniline, interaction first takes place between the piperidine and the quaternary salt with the formation of a certain amount of methylene base and piperidine hydriodide. The reactive methylene base then condenses with the aldehyde or the nitroso-compound to form an intermediate basic product. Lastly, this reacts with the piperidine hydriodide formed in the first stage, regenerating piperidine and yielding the quaternary salt finally obtained.



The view, to which the foregoing considerations thus lead, that the active agents in the condensations of quinaldinium salts are the methylene bases was first expressed on different grounds by Vongerichten and Höfchen (*Ber.*, 1908, **41**, 3054). They showed that quinaldine ethiodide behaves towards cold aqueous alkalis differently from the quaternary salts of quinoline, giving an oil

insoluble in water which readily dissolves in ether or benzene. They regarded this oil as a methylene base (V) formed thus:

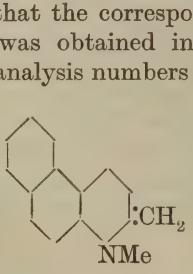


(V.)

and showed that it reacted with quinoline ethiodide in alcoholic solution to form ethyl-red (1 : 1′-diethyl*iso*cyanine iodide). The importance of the part played by the methylene bases is also advocated by König (*Ber.*, 1922, **55**, 3301).

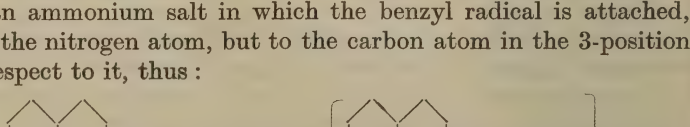
We have made some experiments to test the view of the mechanism of the condensation of quinaldinium salts with aldehydes and with nitroso-compounds explained above and have been able to obtain evidence demonstrating the possibility of each step in the scheme suggested.

(i). *Methylene Bases.*—The oils formed by the action of alkalis on quinaldine alkyliodides cannot be obtained analytically pure. We have been able to confirm the view that they are methylene bases by examining the product similarly got from β-naphthaquinaldine methiodide, which is crystalline (Vongerichten and Höfchen, *loc. cit.*, state that the corresponding ethyl derivative is solid). This substance was obtained in bright yellow platelets which gave on complete analysis numbers agreeing excellently with the formula VI.



(VI.)

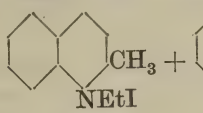
Further evidence respecting the oil resulting from the action of alkalis on quinaldine ethiodide has been obtained by examining its behaviour towards benzyl iodide. If the oil is a methylene base, it contains the grouping –Ṅ·Ċ:Ċ– and, in view of the exceedingly interesting work of Robinson (J., 1916, **109**, 1038; see also Armit and Robinson, J., 1922, **121**, 829) on the addition of alkyl halides to this grouping, it should then combine with benzyl iodide to form an ammonium salt in which the benzyl radical is attached, not to the nitrogen atom, but to the carbon atom in the 3-position with respect to it, thus:

(i)


(VII.)

The actual products of the reaction were, however, quinaldine ethiodide and *dibenzylquinaldine ethiodide*.

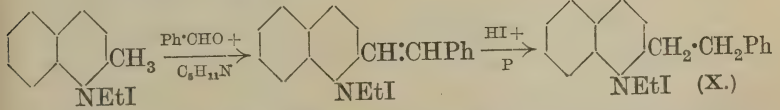
This shows that the first stage of the reaction must proceed as shown above (i), but that the primarily formed benzylquinaldine ethiodide and unchanged methylene base then interact to yield quinaldine ethiodide and the benzylmethylene base (VIII) (reaction ii), and the latter then reacts again with benzyl iodide according

(ii) (V) + (VII) ⇌  (VIII.)

(iii) (VIII) + CH_2PhI =  (IX.)

to Robinson's scheme (reaction iii), giving the final product, dibenzylquinaldine ethiodide (IX). The formation of quinaldine ethiodide in the reaction is a sufficient proof of the occurrence of an interaction of the type (ii).

To show that the last stage (iii) in this series of reactions can be realised, we prepared benzylquinaldine ethiodide (X) as indicated in the following scheme :



and allowed the base obtained from it with sodium hydroxide to react with benzyl iodide. We found that dibenzylquinaldine ethiodide was again produced.

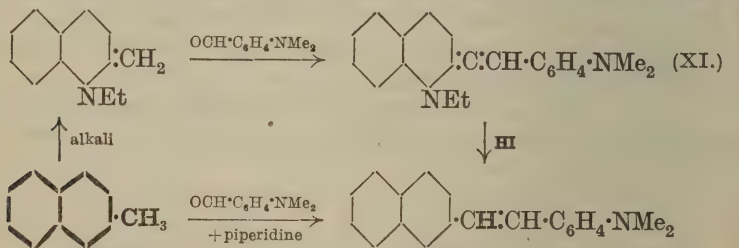
Dibenzylquinaldine was previously unknown, but it has been synthesised by Mr. A. T. Akers and one of us (following paper). Its ethiodide proved to be identical with the product obtained by the action of benzyl iodide on the methylene base; the constitution of that product was therefore conclusively established.

It is thus shown that when the bases obtained by the action of alkalis on quinaldine ethiodide, or benzylquinaldine ethiodide, are treated with benzyl iodide, quaternary ammonium iodides are formed in which the benzyl groups are attached, not to the nitrogen atom, but to a carbon atom in the 3-position with respect to it. This demonstrates that these substances must contain as their essential reactive constituents bases in which an ethylenic linking is conjugated with the nitrogen atom thus : –N·C:C–, that is, they must contain, at any rate under the conditions of these experiments, the methylene bases of the type V and VIII.

The behaviour of 1-ethyl-2-methylene-1 : 2-dihydroquinoline towards benzyl iodide corresponds closely with that of 1 : 3 : 3-trimethyl-2-methyleneindoline towards methyl iodide (Zatti and Ferratini, *Gazzetta*, 1891, **21**, 326; Plancher, *Ber.*, 1898, **31**, 1492):

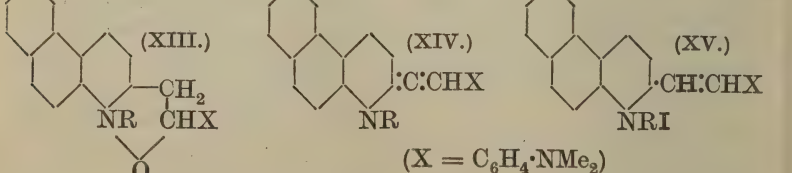
$$C_6H_4\!<\!\begin{matrix}CMe_2\\NMe\end{matrix}\!>\!C{:}CH_2 \xrightarrow{MeI} C_6H_4\!<\!\begin{matrix}CMe_2\\NMe\end{matrix}\!>\!C{:}CMe_2.$$

(ii). *Condensation of the Methylene Bases with Aldehydes.*—When an alcoholic solution of the methylene base from quinaldine ethiodide (1-ethyl-2-methylene-1 : 2-dihydroquinoline) is heated with dimethylaminobenzaldehyde, condensation takes place readily *without the addition of any catalyst.* The compound produced was, however, very unstable and could not be isolated, but it reacted immediately with one equivalent of hydrogen iodide to give the same purple dye, dimethylaminostyrylquinoline ethiodide (XII), as is produced when quinaldine ethiodide is heated with dimethyl-



aminobenzaldehyde in presence of piperidine. It is therefore probable that the substance first formed has the constitution XI.

This conclusion was confirmed by an examination of the condensation products obtained from the methylene bases derived from β-naphthaquinaldine methiodide and ethiodide, which are more stable and more easily manipulated. They are deposited from the reaction mixture as sparingly soluble, scarlet powders and have compositions closely approximating to those required by the formula XIV.



(X = C_6H_4·NMe_2)

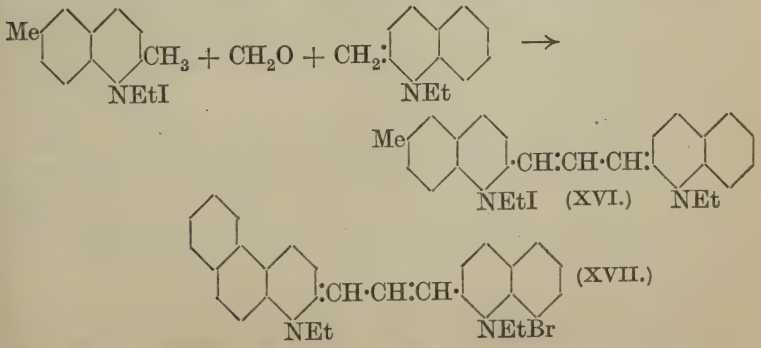
The analyses show that they cannot contain oxygen as an essential constituent. They are therefore not betaine-like compounds of the

formula XIII (although these may well form the primary products of the reaction). They are immediately converted by hydriodic acid into the purple dyes of the formula XV, which are also formed by treating β-naphthaquinaldine alkyliodides with dimethylaminobenzaldehyde and piperidine. If, as appears certain from the foregoing observations, the purple dyes are formed from the scarlet condensation products by the simple addition of the elements of hydrogen iodide, this addition can only have taken place in accordance with Robinson's scheme. The hydrogen atom added will be that indicated by the clarendon type in formula XV and the constitution of the scarlet condensation products must be represented by formula XIV. They are thus allene derivatives and have the instability characteristic of substances containing the allene grouping.

Since these allene bases proved capable of abstracting hydrogen iodide from piperidine hydriodide, forming the purple dyes (XV), the evidence for the scheme on page 2467 seems complete.

(iii). *Production of Unsymmetrical* 2 : 2′-*Carbocyanines*.—The methods previously available for the formation of dyes of the pinacyanole type enable the symmetrical members only of the class to be prepared, that is, those in which the heterocyclic nuclei are similar and similarly substituted. By taking advantage, however, of the great reactivity of the methylene bases, it is possible to prepare unsymmetrical 2 : 2′-carbocyanines.

We found in the first place that the methylene base obtained from quinaldine ethiodide reacts with formaldehyde and quinaldine ethiodide to form pinacyanole. We then treated the same methylene base with formaldehyde and *p*-toluquinaldine ethiodide and thus obtained the unsymmetrical monosubstituted pinacyanole, 6-methyl-1 : 1′-diethyl-2 : 2′-carbocyanine iodide (XVI), which acts as an exceedingly powerful photographic sensitiser for the red.



In a similar manner with β-naphthaquinaldine ethobromide and

formaldehyde, the methylene base gave the unsymmetrical carbocyanine (XVII).

Similar condensations could probably be also effected between the methylene bases, formaldehyde, and other quaternary salts containing a reactive methylene group such as lepidine ethiodide or 1-methylbenzthiazole ethiodide. This method of preparing unsymmetrical carbocyanines is being investigated more fully.

Experimental.

1-*Methyl*-2-*methylene*-1 : 2-*dihydro*-β-*naphthaquinoline* (VI).—The yellow base precipitated by the addition of sodium hydroxide to an ice-cold 1—2% solution of β-naphthaquinaldine methiodide was extracted with ether and the ethereal solution, after drying with potassium carbonate, was concentrated until solid just began to separate. On cooling rapidly, the methylene base was deposited as bright yellow platelets, darkening at 80° and gradually decomposing above that temperature (Found: C, 87·4, 87·1; H, 6·3, 6·3; N, 6·65, 6·6. $C_{15}H_{13}N$ requires C, 86·95; H, 6·3; N, 6·8%). The substance becomes bright green on exposure to air. In an exhausted desiccator decomposition is slower, but even under these conditions a tar is formed in a few days.

Condensation of the Methylene Bases with Dimethylaminobenzaldehyde.—The methylene base from β-naphthaquinaldine ethiodide (1·75 g.) was boiled for 1 hour with *p*-dimethylaminobenzaldehyde (0·75 g.) dissolved in rectified spirit (60 c.c.). The product separated, partly as a scarlet powder, partly as a nodular deposit on the flask which had an eosin-like lustre and gave the scarlet powder when ground up. It dissolves easily in benzene or chloroform, but is practically insoluble in the other common solvents (Found: C, 84·8, 84·8; H, 6·8, 6·95; N, 7·5, 7·45. $C_{25}H_{24}N_2$ requires C, 85·4; H, 6·8; N, 7·9%).

The methylene base from β-naphthaquinaldine methiodide and dimethylaminobenzaldehyde gave a very similar product (Found: C, 85·5, 84·4, 85·5; H, 6·4, 6·5, 6·6; N, 7·5, 7·6, 7·3, 7·7. $C_{24}H_{22}N_2$ requires C, 85·2; H, 6·5; N, 8·3%).

Action of Hydriodic Acid on the Condensation Products.—The red powder (0·62 g.) prepared in the above manner from β-naphthaquinaldine ethiodide was treated with 1 mol. of hydriodic acid (0·23 c.c. of acid, b. p. 126°) in hot alcohol. On cooling, *p*-dimethylaminobenzylidene-β-naphthaquinaldine (0·73 g.) crystallised, m. p. 227—235°.

For comparison, β-naphthaquinaldine ethiodide (1·75 g.) and dimethylaminobenzaldehyde (0·75 g.) were boiled in alcoholic solution with piperidine (3 drops) for 2 hours. On cooling the

resulting red solution the dye was deposited as lustrous needles, m. p. 231—235° (decomp.) (Found : I, 26·45. $C_{25}H_{25}N_2I$ requires I, 26·3%). The product thus formed was identical with that obtained by the addition of hydrogen iodide to the red powder; mixed m. p. 228—235°. Similarly, the methylene base from quinaldine ethiodide (5 g.) was boiled with *p*-dimethylaminobenzaldehyde (2 g.) in alcoholic solution (50 c.c.) for 20 minutes. After cooling and addition of hydriodic acid (1·2 c.c., b. p. 126°), the mixture became red and dimethylaminobenzylidenequinaldine ethiodide gradually crystallised, m. p. 247—248°, mixed m. p. with the compound formed by the condensation of quinaldine ethiodide with dimethylaminobenzaldehyde in presence of piperidine 247—248° (Found : I, 29·3, 29·6. Calc., I, 29·5%).

Action of Piperidine Hydriodide on the Condensation Products.—To an alcoholic solution of piperidine hydriodide, prepared by adding a quantity of hydriodic acid just short of that required for neutralisation to piperidine (1·24 g.), was added the scarlet powder (3 g.) obtained from dimethylaminobenzaldehyde and the methylene base from β-naphthaquinaldine methiodide. After heating for a few minutes, the solution became purple-red and on cooling crystals (3·9 g.) were deposited. Recrystallised from pyridine, the substance was obtained as lustrous green platelets, m. p. 237—239°, which proved to be identical with the dye obtained by condensing β-naphthaquinaldine methiodide with dimethylaminobenzaldehyde by means of piperidine; mixed m. p. 238—239° (Found : I, 27·2. Calc., I, 27·25%).

Addition of Benzyl Iodide to 1-*Ethyl*-2-*methylene*-1 : 2-*dihydroquinoline.**—The methylene base (1·65 g.) from quinaldine ethiodide was heated for 30 minutes with benzyl iodide (2 g.) in benzene (30 c.c.). On cooling, dark reddish-purple crystals (1·7 g.) were deposited consisting of quinaldine ethiodide, dibenzylquinaldine ethiodide (IX), and some *iso*cyanine. The last was removed by extracting with acetone in a Soxhlet extractor and the two ethiodides were then separated by treatment with cold chloroform. Dibenzylquinaldine ethiodide dissolved and quinaldine ethiodide was left. The quinaldine ethiodide had m. p. 238°, mixed m. p. with a specimen of the salt prepared directly from quinaldine and ethyl iodide 236° (Found : C, 48·1; H, 4·6. Calc., C, 48·2; H, 4·6%).

Dibenzylquinaldine ethiodide, obtained by recrystallising the residue left on evaporation of the chloroform from methyl alcohol, formed yellow prisms, m. p. 214—216° (Found : I, 26·5, 26·6.

* In the work described in this and the following section we received assistance from Mr. A. T. Akers.

$C_{26}H_{26}NI$ requires I, 26·5%). The compound proved to be identical with that obtained from dibenzylacetone and *o*-aminobenzaldehyde (see following paper); mixed m. p. 216°.

Benzylquinaldine Ethiodide.—Quinaldine ethiodide (5 g.) dissolved in alcohol (30 c.c.) was heated for 20 minutes with benzaldehyde (2 c.c.) and piperidine (2 drops). On cooling, benzylidenequinaldine ethiodide was deposited in yellow needles, m. p. 227·5—228° * (Found: I, 32·5. Calc., I, 32·8%). It was reduced to *benzylquinaldine ethiodide* by heating 1·25 g. under reflux with hydriodic acid saturated at 0° (7 c.c.), glacial acetic acid (4 c.c.), and red phosphorus (0·2 g.) for 10 hours. The liquid was evaporated under diminished pressure, a little periodide which had separated was removed, and ether was added, when a rapidly solidifying oil was deposited. Crystallised from methyl alcohol, the compound gave yellow needles, m. p. 172—173° (Found: C, 58·4; H, 5·05. $C_{19}H_{20}NI$ requires C, 58·6; H, 5·1%). This salt was also prepared by heating benzylquinaldine (Heyman and Königs, *Ber.*, 1883, **16**, 2606) with the equivalent quantity of ethyl iodide for 90 hours at 100°, but since benzylquinaldine is not readily obtainable the first described method is the better.

Treated with sodium hydroxide and ether, benzylquinaldine ethiodide yielded an anhydro-base which, treated with benzyl iodide in benzene solution for 15 hours in the cold followed by 30 minutes' boiling, gave dibenzylquinaldine ethiodide, m. p. 213·5°, identical with the product obtained from dibenzylquinaldine, or from the methylene base from quinaldine ethiodide.

6-*Methyl*-1 : 1′-*diethylcarbocyanine Iodide.*—The methylene base (3·4 g.) from quinaldine ethiodide was heated for 20 minutes with *p*-toluquinaldine ethiodide (6·3 g.) and 37% formalin (1·5 c.c.) in boiling alcoholic solution (80 c.c.). A purple solution was formed which deposited felted masses of crystals on standing. These were treated with sulphur dioxide in hot methyl-alcoholic solution to decompose the periodide present and then recrystallised twice from methyl alcohol (Found: I, 25·5. $C_{28}H_{27}N_2I$ requires I, 25·7%). The dye sensitises a gelatino-bromide plate up to λ 6950 for moderate exposures with maxima at λ 6400 and λ 5500.

5 : 6-*Benzo*-1 : 1′-*diethylcarbocyanine Bromide* (XVI).—The methylene base from quinaldine ethiodide (5 g.) was heated for 20 minutes with β-naphthaquinaldine ethobromide (5 g.) in alcoholic solution (80 c.c.) and 40% formalin solution (2·5 c.c.). On cooling, the crude dye was deposited as a purple, amorphous

* Vongerichten and Höfchen, who prepared the compound by the addition of ethyl iodide to benzylidenequinaldine, give the m. p. as 216° (*Ber.*, 1908, **41**, 3058).

powder. Purified by repeated crystallisation from methyl alcohol, it formed needles with a green metallic lustre giving a blue alcoholic solution. The air-dried product apparently contained a molecule of methyl alcohol of crystallisation. On attempting to remove this by heating in a vacuum at 110°, the compound lost bromine, presumably as ethyl bromide. The air-dried product was therefore analysed (Found: C, 70·2; H, 5·8; Br, 15·1. $C_{29}H_{27}N_2Br,CH_4O$ requires C, 69·9; H, 6·0; Br, 15·5%).

The absorption spectrum in alcoholic solution is of the usual carbocyanine type with a main and two subsidiary bands. The bands are intermediate in position between the corresponding bands of pinacyanole and the carbocyanine from β-naphthaquinaldine ethobromide (5 : 6 - 5′ : 6′ - dibenzo - 1 : 1′ - diethylcarbocyanine bromide).

	Main band.	First subsidiary band.	Second subsidiary band.
Pinacyanole (1 : 1′-Diethylcarbocyanine iodide)	6070 Å	5625 Å	5192 Å
5 : 6-Benzo-1 : 1′-diethylcarbocyanine bromide	6250	5750	5350
5 : 6-5′ : 6′-Dibenzo-1 : 1′-diethylcarbocyanine bromide	6380	5880	5500

Our thanks are due to the Department of Scientific and Industrial Research for a grant which has enabled one of us (R. R.) to take part in this work.

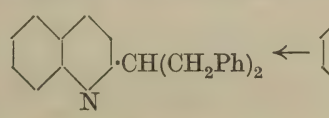
University Chemical Laboratory,
Cambridge.

[*Received, August 1st*, 1925.]

CCCXXXVIII.—*Dibenzylquinaldine.*

By William Hobson Mills and Arnold Thomas Akers.

As described in the foregoing paper, the action of benzyl iodide on the methylene base obtained by the action of alkalis on quinaldine ethiodide resulted in the production of a compound, which from its composition and method of formation was regarded as the ethiodide of dibenzylquinaldine (I).

(I.)  (II.)

To confirm that view of its constitution the synthesis of this previously unknown base was undertaken from *o*-aminobenzaldehyde and dibenzylacetone (II), according to the general method of

Friedländer for the synthesis of bases of the quinoline series (*Ber.*, 1882, **15**, 2574). Dibenzylacetone, which also has not been previously described, could not be obtained by the ketone fission of dibenzylacetoacetic ester, hydrolysis of which under various conditions gave only dibenzylacetic acid. It was, however, readily prepared by treating the amide of dibenzylacetic acid (Schneidewind, *Ber.*, 1888, **21**, 1328) with a large excess of magnesium methyl iodide:

$$(CH_2Ph)_2CH\cdot CO\cdot NH_2 \xrightarrow{MgMeI} (CH_2Ph)_2CH\cdot COMe.$$

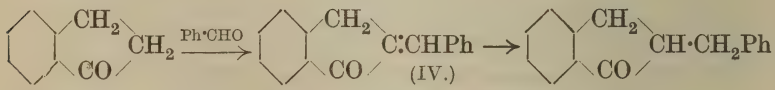
Both this reaction and the Friedländer synthesis proceeded smoothly and the ethiodide of the resulting dibenzylquinaldine proved to be identical with the compound obtained by the action of benzyl iodide on the methylene base. The interpretation of the course of this interaction explained in the foregoing paper was thus established.

In preparing dibenzylacetyl chloride for the purpose of obtaining the corresponding amide the observation was made that this acid chloride lost hydrogen chloride with remarkable ease when heated, forming a compound which was evidently benzylhydrindone (III), since it had ketonic properties, forming a *semicarbazone*.



(III.)

A proof of its constitution was obtained by showing that it was also formed by reduction of benzylidenehydrindone (IV) (Kipping, J., 1894, **65**, 498), a method of formation which leaves no doubt as to its structure.



We subsequently found that the facility with which dibenzylacetyl chloride lost hydrogen chloride had already been observed by Leuchs, Wutke, and Gieseler (*Ber.*, 1913, **46**, 2200) and that they had also demonstrated the constitution of the product, although in a less simple manner.

Experimental.

Dibenzylacetamide.—When a solution of acetoacetic ester in absolute alcohol was treated with sodium ethoxide (1 mol.) and benzyl chloride (1 mol.) and the mixture after completion of the reaction was treated again in the usual way with the same reagents (1 mol. of each), the principal product was not dibenzylacetoacetic

ester * but dibenzylacetic ester, b. p. 209°/19 mm. (Found : C, 80·5; H, 7·4. Calc., C, 80·6; H, 7·5%). The ester was readily hydrolysed by hot dilute alcoholic potash to dibenzylacetic acid, and we found this a more convenient method of preparing the acid than the hydrolysis of dibenzylmalonic ester (Bischoff and Siebert, *Annalen*, 1887, **239**, 92).

To obtain the acid chloride (compare Leuchs, Wutke, and Gieseler, *loc. cit.*) the acid was heated on the water-bath for 4 hours with a slight excess of thionyl chloride. The product was then distilled rapidly under diminished pressure, when a nearly colourless oil, b. p. 197°/12 mm., was obtained (Found : Cl, 13·5. Calc., Cl, 13·7%). The acid amide (compare Schneidewind, *loc. cit.*) was obtained by pouring the crude acid chloride, without removal of the slight excess of thionyl chloride, into a large excess of ammonia (*d* 0·88) at 0—5°. The precipitated amide after crystallisation from benzene had m. p. 128—129° (Found : C, 80·1; H, 7·1; N, 5·8. Calc., C, 80·3; H, 7·2; N, 5·9%). In this manner 30 g. of recrystallised amide were obtained from 40 g. of acid.

as-*Dibenzylacetone*, $(C_6H_5{\cdot}CH_2)_2CH{\cdot}CO{\cdot}CH_3$.—To a solution of magnesium (14·8 g.) in methyl iodide (40 c.c.) and anhydrous ether was added solid dibenzylacetamide, and the mixture was boiled for 18 hours. After decomposition of the magnesium compound with ice and dilute sulphuric acid the ethereal layer was separated. On evaporation of the ether the *ketone* was left as an oil, b. p. 120—122°/16 mm. (Found : C, 85·5; H, 7·65. $C_{17}H_{18}O$ requires C, 85·7; H, 7·6%). Yield 21 grams.

Benzylidenedibenzylacetone, $(C_6H_5{\cdot}CH_2)_2CH{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_5$.—To an alcoholic solution (150 c.c.) of dibenzylacetone (3 g.) and benzaldehyde (1·3 g.), 10% aqueous sodium hydroxide (3 c.c.) was added, and the mixture left for 3 days. The crystalline precipitate formed was recrystallised from alcohol; m. p. 66—67° (Found : C, 88·6; H, 6·7. $C_{24}H_{22}O$ requires C, 88·4; H, 6·75%).

Dibenzylquinaldine (I).—To an alcoholic solution of *o*-aminobenzaldehyde (1 part) and dibenzylacetone (2 parts) a little solid potassium hydroxide was added and the mixture was boiled for 5 hours. Water was then added and the alcohol evaporated, when the product was deposited as a pasty mass which, after keeping for some days in a desiccator, partly crystallised. The crystals, separated and recrystallised from methyl alcohol, gave colourless needles, m. p. 74° (Found : C, 89·4; H, 6·5; N, 4·4. $C_{24}H_{21}N$ requires C, 89·2; H, 6·5; N, 4·3%). Yield 50%.

Dibenzylquinaldine Methiodide.—Dibenzylquinaldine was heated

* This was obtained by Fittig and Christ (*Annalen*, 1892, **268**, 124) by treating acetoacetic ester with 1 or 1¼ mols. of sodium ethoxide and benzyl chloride.

with excess of methyl iodide for 24 hours at 100°. The crystalline deposit formed separated from methyl alcohol in yellow prisms, m. p. 204° (Found: I, 27·5. $C_{25}H_{24}NI$ requires I, 27·3%).

Dibenzylquinaldine ethiodide was prepared similarly to the methiodide except that the heating was continued for 48 hours. Yellow prisms, m. p. 215—216° (Found: C, 64·9; H, 5·5; I, 26·7. Calc., C, 65·1; H, 5·4; I, 26·5%). The compound was identical with that obtained by the action of benzyl iodide on 1-ethyl-2-methylene-1 : 2-dihydroquinoline.

2-*Benzyl*-1-*hydrindone*.—Similarly to Leuchs, Wutke, and Gieseler (*loc. cit.*), we found that if in the preparation of dibenzylacetyl chloride, phosphorus pentachloride was employed, or if when using thionyl chloride the distillation was carried out too slowly or at too high a pressure, the chief product was benzylhydrindone (Found: C, 86·5; H, 6·3. Calc., C, 86·5; H, 6·3%). The *semicarbazone*, crystallised from alcohol, had m. p. 198—199° (Found: N, 15·2. $C_{17}H_{17}ON_3$ requires N, 15·05%).

Reduction of Benzylidenehydrindone.—Benzylidenehydrindone was prepared as described by Kipping (J., 1894, **65**, 480) except that thionyl chloride was used instead of phosphorus pentachloride for the preparation of phenylpropionyl chloride and zinc chloride was employed instead of alcoholic potassium hydroxide for the condensation of hydrindone with benzaldehyde, equimolecular quantities of the latter two compounds being heated together for 8 hours on the water-bath with a little anhydrous zinc chloride, and the product separated by dissolving in alcohol and pouring into cold water. The reduction of benzylidenehydrindone to benzylhydrindone was carried out as follows: Benzylidenehydrindone (10 g.) was dissolved in a mixture of methyl and ethyl alcohol, and 3·3% sodium amalgam (300 g.) was added gradually during 4 hours, the mixture being kept neutral to phenolphthalein by the regulated addition of 50% acetic acid. After evaporation of the alcohol, water was added and the product was extracted with ether. It boiled at 222°/18 mm. and its identity with the compound formed by loss of hydrogen chloride from dibenzylacetyl chloride was shown by conversion into the semicarbazone (Found: C, 73·5; H, 5·6. Calc. for $C_{17}H_{17}ON_3$, C, 73·1; H, 6·1%). The m. p. of this semicarbazone as well as the "mixed m. p." with the semicarbazone of the ketone obtained from diphenylacetyl chloride was 198—199°.

The analyses for carbon, hydrogen and nitrogen recorded in this paper were carried out by Mr. F. H. Flack.

University Chemical Laboratory,
Cambridge. [*Received, August 1st*, 1925.]

CCCXXXIX.—*The Resolution of an Asymmetric Arsenic Compound into its Optically Active Forms.*

By William Hobson Mills and Richard Raper.

In spite of the probability that corresponding compounds of nitrogen, phosphorus, and arsenic possess similar stereochemical configurations, numerous investigations have shown that for some reason it is not possible to demonstrate the molecular dissymmetry of the phosphonium and arsonium compounds in the same simple way as has been done for the quaternary ammonium salts. Thus in the case of the arsonium compounds the attempts to effect resolution carried out by Michaelis (*Annalen*, 1902, **321**, 159) and Winmill (J., 1912, **101**, 718) gave negative results. Similarly, negative evidence only was obtained in attempts to resolve arsine oxides made by Burrows and Turner (J., 1921, **119**, 426), Aeschlimann and McCleland (J., 1924, **125**, 2025), and Aeschlimann (this vol., p. 811), although amine and phosphine oxides are readily resolved (Meisenheimer, *Ber.*, 1908, **41**, 3966; Meisenheimer and Lichtenstadt, *Ber.*, 1911, **44**, 356). The only positive result hitherto recorded is that of Burrows and Turner (*loc. cit.*), who succeeded in obtaining a solution of *d*-phenyl-α-naphthylbenzylmethylarsonium iodide which showed a rotation of $\alpha_D = 0{\cdot}1°$ in a 2-dcm. tube. It seemed to us, therefore, that in order to obtain satisfactory evidence that arsenic can behave as a centre of asymmetry, it would be advisable, in the first instance at any rate, to investigate some other type of compound of the element. We have therefore prepared and examined p-*carboxyphenylmethylethylarsine sulphide* (I), and have found that it can be resolved into enantiomorphous modifications. This compound is closely related in structure to the tertiary amine and phosphine oxides obtained in optically active forms by Meisenheimer; the procedure we have followed for effecting its resolution is, however, different. Meisenheimer made use of the basicity of the oxides for this purpose. Thus, in the case of methylethylaniline oxide, the separation was brought about through the diastereoisomeric salts $\left[\begin{matrix}\text{Ph}\\\text{Me}\end{matrix}\!>\!\text{N}\!<\!\begin{matrix}\text{Et}\\\text{OH}\end{matrix}\right]\text{C}_{10}\text{H}_{14}\text{BrSO}_3$. We thought it advisable that the arsenic atom should be shielded as far as possible from disturbance in the processes of salt formation and decomposition involved in resolution experiments, and therefore chose a compound deriving its salt-forming capacity from a substituent carboxyl group. We regard the presence of the sulphur atom as the essential feature

which enables the molecular asymmetry of the compound to be demonstrated experimentally. The grouping $R_1R_2R_3As{:}S$ forms a chemically indifferent complex, free from the basicity characteristic of the arsine oxides (the sulphide used in these experiments did not form a hydrochloride), and whilst the corresponding oxygen compound shows only a feeble acidity, being presumably an internal salt, $\overset{-}{O}\cdot CO\cdot C_6H_4\cdot \overset{+}{As}MeEt\cdot OH$, this arsine sulphide carboxylic acid is strongly acidic and forms stable salts with the commoner alkaloids.

p-Carboxyphenylmethylethylarsine sulphide (I) was prepared by oxidising *p*-tolylmethylethylarsine (II) to *p*-carboxyphenylmethylethylarsine oxide (III) and treating the hydrochloride of this substance with hydrogen sulphide in aqueous solution (Michaelis,

$$\underset{\text{(II.)}}{CH_3\cdot C_6H_4\cdot As<\begin{matrix}Me\\Et\end{matrix}} \xrightarrow{KMnO_4} \underset{\text{(III.)}}{HO_2C\cdot C_6H_4\cdot As(=O)<\begin{matrix}Me\\Et\end{matrix}} \xrightarrow{H_2S} \underset{\text{(I.)}}{HO_2C\cdot C_6H_4\cdot As(=S)<\begin{matrix}Me\\Et\end{matrix}}$$

Annalen, 1902, **320**, 306). It was resolved by the fractional crystallisation of its brucine and morphine salts. The specific rotation of the brucine salt of the racemic acid is $[\alpha]^{20°}_{5461} = -5{\cdot}8°$. During twelve recrystallisations of the salt from water its specific rotation fell steadily until the value $[\alpha]^{20°}_{5461} = -19{\cdot}65°$ was reached, although analyses showed that its composition remained unchanged. Two further recrystallisations gave values of $[\alpha]^{20°}_{5461} = -19{\cdot}5°$ and $-19{\cdot}6°$ respectively. The resolution was therefore considered to be complete, and the lævorotatory acid obtained from the salt after removal of the brucine was regarded as the optically pure *l*-acid. Its specific rotation was not altered by recrystallisation, and it gave the following polarimetric constants:

$$[\alpha]^{20°}_{5780} = -19{\cdot}1°. \quad [M]^{20°}_{5780} = -52° \text{ (in alcohol).}$$
$$[\alpha]^{20°}_{5461} = -21{\cdot}6°. \quad [M]^{20°}_{5461} = -59° \text{ (in alcohol).}$$

The morphine salt was fractionated by dissolving it in alcohol and precipitating with ether. After four recrystallisations, a specific rotation of $-50°$ for the mercury green line was attained, and six further recrystallisations failed to change this. The *d*-acid set free from this salt gave values for the specific rotation which were, within the limits of the errors of observation, equal and opposite to those found for the *l*-acid.

Experimental.

p-*Tolylmethyliodoarsine.*—*p*-Tolylarsenious oxide (50 g.) is dissolved in a solution of sodium hydroxide (27·7 g.) in water (55 c.c.) and rectified spirit (220 c.c.), the liquid being kept cool. The solution is placed in a flask attached to a reflux condenser, and methyl iodide (28 c.c.) is added. After standing 24 hours, the alcohol is distilled off, the residue acidified with hydrochloric acid, potassium iodide (50 g.) added, and the solution saturated with sulphur dioxide. The p-*tolylmethyliodoarsine* separates as a dark-coloured oil, which is taken up in chloroform, dried with calcium chloride, and distilled in a vacuum. The distillate is a golden-yellow oil, b. p. 163—165°/12 mm., which solidifies on standing to canary-yellow needles, m. p. 29° (Found: C, 31·2; H, 3·1; I, 41·15. $C_8H_{10}IAs$ requires C, 31·2; H, 3·05; I, 41·25%). Yield, 50 g.

p-*Tolylmethylethylarsine.*—*p*-Tolylmethyliodoarsine (100 g.) is dissolved in dry benzene (100 c.c.) and added slowly to a Grignard reagent prepared from magnesium turnings (10·4 g.), dry ether (200 c.c.), and ethyl bromide (31 c.c.). When the addition is completed, the liquid is boiled 2 to 3 hours and poured on to ice. The whole is acidified with dilute sulphuric acid, and the ethereal layer separated off and dried with sodium sulphate. The solvents are removed, and the *arsine* distilled in a vacuum. It is a colourless oil, b. p. 117°/15 mm. Yield, 50 g. (Found: C, 57·1; H, 7·2. $C_{10}H_{15}As$ requires C, 57·1; H, 7·1%).

dl-p-*Carboxyphenylmethylethylarsine Sulphide* (I).—*p*-Tolylmethylethylarsine (25 g.) is treated gradually with shaking with a solution of potassium permanganate (50 g.) in water (2 litres). The mixture is placed in a thermostat at 35° until the oxidation is complete (7—10 days). The excess of permanganate is removed by adding alcohol, and the filtrate from the manganese dioxide is acidified with hydrochloric acid and evaporated to dryness. The residue is taken up in water (400 c.c.) and the solution saturated with hydrogen sulphide. The precipitated *sulphide*, recrystallised from water, forms lustrous needles, m. p. 183°. Yield 10—12 g. (Found: C, 44·0; H, 4·8; As, 27·8. $C_{10}H_{13}O_2SAs$ requires C, 44·1; H, 4·8; As, 27·6%). The compound is readily soluble in alcohol or chloroform, but insoluble in benzene, light petroleum, or ether.

Brucine salt. Brucine (50 g.) and *dl*-acid (40 g.) were heated under reflux in absolute alcohol (500 c.c.) for 2 hours. The crystals deposited on cooling were collected and fractionally crystallised

from water. The following table shows the progress of the resolution:

No. of recryst.	Gram of salt in chloroform (25 c.c.).	$\alpha^{20°}_{5461}$. $l=2$ dcm.	$[\alpha]^{20°}_{5461}$.	No. of recryst.	Gram of salt in chloroform (25 c.c.).	$\alpha^{20°}_{5461}$. $l=2$ dcm.	$[\alpha]^{20°}_{5461}$.
Salt of *dl*-acid*	0·5000	−0·23°	− 5·8°	7	0·4128	−0·55	−16·6
1	0·5322	−0·30	− 7·1	8	0·5167	−0·71	−17·2
2	0·6120	−0·49	−10·9	9	0·5810	−0·81	−17·4
3	0·5252	−0·52	−12·3	10	0·5625	−0·84	−18·6
4	0·5730	−0·54	−11·8	11	0·5480	−0·81	−18·5
5	0·5837	−0·68	−14·8	12	0·5025	−0·79	−19·65
6	—	—	—	13	0·5057	−0·75	−19·5
				14	0·5163	−0·81	−19·6

* This was obtained by dissolving 0·296 g. of brucine and 0·204 g. of *dl*-acid in 25 c.c. of chloroform. The rotation of 0·296 g. of brucine in 25 c.c. of chloroform is $\alpha_{5461} = 3·37°$.

The composition of the salt remained constant throughout the fractionation, the values obtained from the crops in the 1st, 4th, 5th, 7th, and 12th recrystallisations being C, 58·4, 58·2, 58·0, 58·1, 58·3; H, 6·0, 6·2, 6·15, 6·1, 6·0; N (7th recryst.), 4·9; As (7th recryst.), 11·4. $C_{33}H_{39}O_6N_2SAs$ requires C, 59·5; H, 5·9; N, 4·2; As, 11·3%.

l-p-*Carboxyphenylmethylethylarsine Sulphide.*—The final fraction of the brucine salt was shaken with excess of sodium hydroxide and chloroform, and the aqueous layer extracted four times with chloroform to ensure complete removal of the brucine. The solution of the sodium salt was kept ice-cold and acidified with hydrochloric acid, the l-*acid* collected, washed with water, and dried. It was recrystallised by dissolving in chloroform and precipitating with light petroleum; m. p. 175—177° (Found: C. 44·0; H, 4·7. $C_{10}H_{13}O_2SAs$ requires C, 44·1; H, 4·8%).

0·5753 g. made up to 50 c.c. with absolute alcohol gave the following measurements in a 6-dcm. tube at 20°:

$$\alpha^{20°}_{5780} = -1·31°;\ [\alpha]^{20°}_{5780} = -19·1°;\ [M]^{20°}_{5780} = -52°.$$
$$\alpha^{20°}_{5461} = -1·49°;\ [\alpha]^{20°}_{5461} = -21·6°;\ [M]^{20°}_{5461} = -59°.$$

Morphine salt. Morphine (40 g.) and *dl*-acid (40 g.) were heated under reflux in absolute alcohol (500 c.c.) for 2 hours. The solution was filtered, allowed to cool, and ether (400 c.c.) was added. The morphine salt (64 g.) was fractionated by dissolving in absolute alcohol, filtering, adding ether until the solution became turbid, warming, and allowing to stand. The following table shows the progress of the resolution:

No. of recryst.	Gram of salt in alcohol (25 c.c.).	α_{5461}. $l=2$.	$[\alpha]_{5461}$.	No. of recryst.	Gram of salt in alcohol (25 c.c.).	α_{5461}. $l=2$.	$[\alpha]_{5461}$.
Salt of *dl*-acid*	0·55	−2·86°	−64·9°	5	0·3282	−1·30°	−49·6°
1	0·3000	−1·36	−56·8	6	—	—	—
2	0·4714	−2·01	−53·4	7	0·2980	−1·23	−51·6
3	0·3572	−2·28	−53·8	8	—	—	—
4	0·3104	−1·26	−50·8	9	0·2077	−0·79	−47·5
				10	0·2100	−0·86	−51·1

* Obtained by dissolving 0·28 g. of morphine and 0·27 g. of *dl*-acid in 25 c.c. of absolute alcohol.

d-p-*Carboxyphenylmethylethylarsine Sulphide*.—The final fraction of the morphine salt was shaken with chloroform and successive quantities of dilute sulphuric acid until the latter extracted no more morphine. The chloroform solution was dried with anhydrous sodium sulphate, and the d-*acid* was precipitated by adding light petroleum.

0·3530 g. made up to 15 c.c. with absolute alcohol gave the following measurements in a 2-dcm. tube at 20° :

$\alpha^{20°}_{5780} = +0·90°$; $[\alpha]^{20°}_{5780} = +19·1°$; $\alpha^{20°}_{5461} = +0·98°$; $[\alpha]^{20°}_{5461} = +21°$.

The acid was recrystallised by dissolving in absolute chloroform and precipitating with light petroleum; m. p. 175—176°.

0·2560 g. made up to 15 c.c. with absolute alcohol gave the following measurements in a 2-dcm. tube at 20° :

$\alpha^{20°}_{5780} = +0·64°$; $[\alpha]^{20°}_{5780} = +18·7°$; $[M]^{20°}_{5780} = +51°$.
$\alpha^{20°}_{5461} = +0·76°$; $[\alpha]^{20°}_{5461} = +22·2°$; $[M]^{20°}_{5461} = +60°$.
$\alpha^{20°}_{4359} = +1·33°$; $[\alpha]^{20°}_{4359} = +39·4°$; $[M]^{20°}_{4359} = +107°$.

(Found : C, 44·25, 44·3; H, 4·9, 4·8. $C_{10}H_{13}O_2SAs$ requires C, 44·1; H, 4·8%).

The authors wish to express their thanks to the Chemical Society for a grant towards the expenses of this research, and also to the Department of Scientific and Industrial Research for a maintenance grant made to one of them during part of the time occupied in carrying out the work.

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CCCXL.—*The Production of Oxide Films on Copper at the Ordinary Temperature.*

By Ulick Richardson Evans.

When copper is exposed to air at *high temperatures*, the oxidation proceeds rapidly at first, but soon slows down, since the film first produced restricts the access of oxygen to the metal below; nevertheless a layer of scale of appreciable thickness is quickly formed. At low temperatures, diffusion through an oxide film is much slower, and thickening soon becomes sluggish; the films produced at about 200° have thicknesses comparable with the wave-length of light, and interference tints therefore appear on the surface. The sequence commences: Brown, reddish-mauve, blue, greenish-silver; then follow the "second order" colours yellow, rose, blue, green; one can usually observe a further alternation between rose and green, before the tints pass into the dull pinkish-grey which is probably the characteristic colour of the oxide.

At the *ordinary temperature*, copper can be exposed to dry, pure air for a long time without any visible change at all. It is considered by Tammann that an invisible oxide film at least one molecule thick is formed rapidly, but that this layer is practically impervious to oxygen at low temperatures, and soon ceases to thicken.

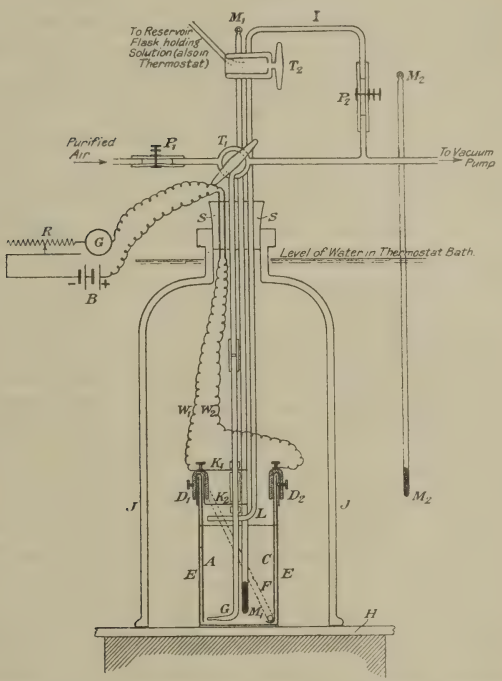
Recently the author (*Ind. Eng. Chem.*, 1925, **17**, 363) found that colours of every hue, due to oxide films, could be produced at the ordinary temperature on copper (and also on brass, lead, zinc, and steel) by the *combined action of oxygen and cathodic treatment*—a combination which seems to render the oxide film less protective, and so allows the rapid attainment of visible thickness. These tints were first noticed on the "aerated zones" of corrosion-specimens exposed to the non-uniform action of oxygen, the electric current being produced by "differential aeration." Afterwards the tints were obtained with current supplied from an external source.

The stimulation of film-formation by a combination of oxidising and reducing conditions had previously been noted by Hinshelwood (*Proc. Roy. Soc.*, 1922, *A*, **102**, 318), who had exposed copper alternately to oxygen and hydrogen at 233°; the oxygen produced a film of oxide, and the hydrogen reduced this to metal; on each successive oxidation, oxygen was taken up with increasing rapidity, probably on account of the porous character of the reduced copper. Similarly Palmer (*ibid.*, 1923, *A*, **103**, 444) found that a mixture of oxygen and hydrogen caused the oxidation of reduced copper more quickly than did oxygen alone. But these experiments all

referred to elevated temperatures, and it seemed desirable to study in greater detail the formation of visible films at the *ordinary temperature.*

Materials and Apparatus.—Kahlbaum's pure electrolytic foil of 1 mm. thickness was employed, the superficial oxide being removed

FIG. 1.



J, *Glass bell-jar.* H, *Ground-glass plate.* S, *Rubber stopper.* W_1, W_2, *Electrical leads.* D_1, D_2, *Brass clamp terminals.* E, *Electrolysis vessel.* A, *Anode.* C, *Cathode.* K_1, K_2, *Supports of stout copper holding air-delivery tube in correct position.* L, *Delivery tube for liquid.* G, *Tube for delivering air, and withdrawing liquid.* M_1, M_2, *Thermometers.* F, *Frame of glass tubing for holding cathode taut.* T_1, *Three-way tap for evacuating flask, and admitting purified air.* T_2, *Three-way tap for admitting and withdrawing liquid.* P_1, P_2, *Screw regulating valves.* B, *Battery (two accumulators).* R, *Variable resistance.* G, *Ammeter.*

with emery (FF).* Kahlbaum's sodium hydroxide, prepared from sodium, was used for the solutions.

The electrolysis was conducted in a rectangular trough (E) $7 \times 5 \times 9{\cdot}5$ cm. (Fig. 1), the electrodes (C and A) being clamped

* Washing the ground surface with alcohol and benzene did not affect the velocity of coloration. Colours can also be obtained on rouge-polished copper.

against the walls of the trough. In the earlier "open-vessel" experiments, this trough stood on the laboratory bench, and the liquid in it was undoubtedly kept in circulation by convection currents, which were perhaps rather exceptionally vigorous, since the work was conducted in very hot weather in a room immediately below the roof. In the "closed-vessel" experiments, the electrolysis vessel, E, was enclosed below the bell-jar, J, which was cemented to the ground-glass plate, H, by tap-grease. The whole apparatus was immersed in a thermostat bath. By suitable operation of the taps T_1 and T_2 it was possible (1) to exhaust the apparatus, (2) to fill the electrolysis vessel with $N/10$-sodium hydroxide from the "reservoir-flask," (3) to draw in purified air (which entered through five vessels containing sodium hydroxide, dilute sulphuric acid, sodium hydroxide, Nessler solution, and lead acetate respectively), and (4) to draw off portions of liquid as required.

Open-vessel Experiments.—Preliminary trials with various solutions indicated that $N/10$-sodium hydroxide was most suitable. At very low current densities (0·1 m.a./sq.cm.), colours could be obtained near the water level, during electrolysis itself. But it was found more convenient to apply a current density sufficient to produce evolution of hydrogen gas over the cathode; the metallic surface, which was then unchanged in appearance when the electrolysis ended, acquired coloration on standing.

In early experiments, electrolysis was continued for 5 minutes at 2·5 m.a./sq.cm. After this time, 10 c.c. of liquid were sucked out so as to lower the water-level, and similar quantities removed at intervals, usually of 3 minutes. When the vessel had been completely emptied, the cathode was always found to be coloured differently in the various zones. The uppermost zone, which had emerged as soon as electrolysis terminated, was unchanged, but below this appeared colours depending on the period of immersion after the end of electrolysis; the order was exactly the same as in high-temperature tinting. Sooner or later the colour ceased to change further, although a prolonged exposure of about 12 hours produced patches of dull brown oxide on the lower parts of the surface.

The alteration in hue occurred *sharply* at each successive position of the water level; the metal, when once it had emerged above the water line, ceased to change colour further, even where it was still wet with a film of liquid, although the immersed portion continued to develop. It was, indeed, found that if, after a portion of the electrode had emerged from the liquid, it was again submerged by reintroduction of liquid into the trough, no further colour change occurred on those parts which had been exposed to the air.

If, immediately after the cessation of electrolysis, part of the

cathode was wiped vigorously with a glass rod, a rubber-tipped rod, or another piece of copper, the part so treated lost its power of colouring, and the place remained unchanged long after the whole of the rest of the cathode had become tinted; when at last a change set in over the wiped area, only a dirty yellowish-grey or brown colour appeared. Vigorous stirring of the liquid also prevented the formation of colours beyond the first brown.

The time required to produce coloration varied considerably in different experiments; and the period which elapsed between grinding and electrolysis seemed to be an important factor. In one case where grinding was performed just before the introduction into the bath, parts of the cathode failed to colour at all. This suggested that the presence of a thin invisible oxide film on the electrode before electrolysis might be favourable to the production of colours. It was difficult, however, to prevent coloration entirely by grinding alone, and attention was directed to the possibility of removing the hypothetical invisible oxide film by acid treatment, just before electrolysis. To prevent reoxidation, it was decided to plunge the cathode into the bath with the acid still adhering; a few drops of acid would quickly be neutralised by the large excess of alkali in the bath. Accordingly, isolated drops of acid were placed on part of the cathode surface; the electrode was then plunged into the electrolysis bath, and the current at once turned on. The parts wetted with acid were clearly distinguishable after the commencement of electrolysis, since hydrogen bubbles occurred here many seconds before they appeared on the main portion (owing, no doubt, to the high local hydrion concentration); the shapes of these areas were sketched on paper. After about 30 seconds, hydrogen evolution became general over the whole surface. When the electrolysis was over, and the copper was allowed to colour, the centre of the acid-treated areas became tinted, but around the limits of the acid-treated areas were belts of unchanged copper, showing no colours whatever. Numerous other experiments, performed in different manners (both with N- and $5N$-acid), gave confirmatory results.

Separate experiments were then made on the action of dilute sulphuric acid (both N and $5N$) on copper covered with a *visible* film of cuprous oxide obtained by heating in air. A drop of acid placed on the oxidised surface produced black, spongy copper (due to the instability of cuprous sulphate); but as the drop spread slowly outwards over the oxidised surface, a zone of clean bright copper was produced *at the edge* of the drop, the copper being precipitated preferentially on the nuclei of spongy copper already present in the central portion. Combining this result with that of the

previous experiment, it becomes evident that *compact copper which is quite free from oxide and from porous copper is not easily rendered colourable by cathodic treatment; but that porous copper, whether produced by the action of acid or by cathodic action on an invisible oxide film, makes the surface readily colourable.*

A strip of freshly ground copper was heated in a flame along the left-hand edge, so as to produce a narrow brown rim, the rest of the strip being unchanged in appearance, although probably covered with an oxide film too thin to give the first oxidation tint. The strip was then subjected to cathodic treatment in the ordinary way, and allowed to colour. The coloration occurred most quickly at the left-hand edge, the colours appearing more and more slowly as the right-hand side was approached. The effect, however, extended far into the region wherein no visible alteration had occurred when the copper was heated. Evidently the presence even of an invisible oxide film is a favourable condition for subsequent cathodic coloration.

Parallel experiments showed that copper which had been ground and heated in dry air for $\frac{1}{2}$ hour at 95° coloured much more quickly, and also more uniformly, than freshly ground copper. The heating at this temperature—in the absence of moisture—did not in itself cause any alteration in the appearance of the copper, and was adopted as preliminary treatment before all the "closed vessel" experiments.

Experiments with non-uniform current density showed that the colouring was essentially independent of the current density.

Closed-vessel Experiments in the Thermostat Apparatus.—When a zinc anode was employed (to avoid the anodic production of oxygen), it was found possible—by continuing the exhaustion of the bell-jar throughout the experiment—to prevent any coloration other than a pale brown. But when the apparatus was filled with purified air, the colours appeared quickly after the termination of electrolysis, showing that the production of tints is not due to any atmospheric impurity, such as hydrogen sulphide.

Under thermostatic conditions, the colours produced without stirring were not uniform, the colour near to each position of the water level being more "advanced" than that below. This was clearly due to the fact that oxygen reached the metal close to the water level more readily than it reached the part well below the surface. A similar lack of uniformity in each zone had been noticed in some of the experiments made in open cells (no doubt when the convection currents were not adequate to circulate the oxygen); but it became a serious problem when the closed-vessel experiments were commenced, for under thermostatic conditions ordinary thermal

convection and also "Adeney streaming" (*Phil. Mag.*, 1923, **45**, 835) were excluded.

To obtain uniformity of oxygen concentration throughout the liquid, it was decided to bubble the air cautiously through the liquid (violent bubbling would destroy the colouring power of the cathode); under any conditions, coloration proceeded up to a point, and then no further change of tint occurred. Experiments wherein four cathodes, which had received electrolytic treatment for different periods, were simultaneously exposed to dissolved oxygen showed that the longer the time of electrolysis, and the more gentle the stirring, the more advanced was the final tint attained. On the other hand, thorough stirring gave brighter and more uniform colour than gentle stirring. In one experiment, conducted at 17·7°, with gentle stirring produced by electrolytic gas (a subsidiary cathode being provided below the anode), the cathode electrolysed for 20 minutes reached the second-order red; that electrolysed for 10 minutes attained greenish-grey (first order); that electrolysed for 5 minutes reached reddish-brown (first order), whilst that electrolysed for only 1 minute was nearly unchanged, being only slightly brown.

A more satisfactory method of obtaining the advanced colours consisted in blowing dried air on to the liquid surface from a tube just touching the liquid; this produced tremors over the surface, without causing bubbles to rise *through* the liquid. In one experiment, four cathodes were subjected to electrolysis for 20, 10, 5, and 2 minutes respectively. Liquid was then withdrawn at intervals, air being blown on to the surface between the occasions of removal at the rate of 200 c.c. per minute; the temperature was kept within 0·1° of 21·7°. The cathode which had received 10 minutes' electrolysis became red-brown in 2 minutes, bluish-mauve in 4 minutes, and blue in 6 minutes. It then passed through green-grey and reached the second-order yellow in 16 minutes, and then passed through pink to bluish-grey, which was the final tint attained. The cathode electrolysed for 20 minutes developed slightly faster, and those electrolysed for 5 minutes or 2 minutes rather slower. But in all cases second-order tints were reached.

Mechanism of Cathode Coloration.—There seems no doubt that the colouring agent is hydrogen stored in the copper; through alternate oxidation and reduction, the film will tend to be more porous than that obtained in the absence of hydrogen, and thus visible thickness will be reached. The charge of hydrogen will depend on the time of electrolysis, but not on the current density (which has little effect on the over-potential, that is, on the supersaturation at the surface); this explains the effect of time of electrolysis on the final tint attained. Stirring and withdrawal into air will allow the hydrogen to escape

before it has done its work, and will thus destroy the colouring power.

It remains to explain why an invisible oxide film is favourable to subsequent coloration. Nearly all heterogeneous reactions commence at nuclei and spread out from them. It seems likely that at *high* temperatures the oxide nuclei produced on metal exposed to air are so close together that the oxide phase extending from the different nuclei soon comes to form a film of practically constant thickness. But at *low* temperatures, the " nucleus number " is doubtless much smaller; if the surface layer consists of ordinary compact copper, the oxidation, extending from sparsely distributed points, will fail to produce a film of constant thickness—at least for a considerable time. But a layer of porous copper with a true surface vastly exceeding the apparent surface will yield a far greater number of nuclei per unit apparent area, and the film formed may then quickly reach an approximately uniform thickness of the order needed to give interference colours. This also explains why wiping the surface (which will remove the spongy copper) destroys the colouring power.

Experiments on the Anodic Oxidation of Copper in N/10-*Sodium Hydroxide at Different Current Densities.*—At 3·5 m.a./sq.cm., oxygen was evolved on the copper anode, which in 16 hours underwent no important change over the immersed portion; but two thin dark lines appeared just above and below the water level, as though the protective oxide film which prevented attack elsewhere had here broken down (the water level is the usual place for such a break-down. Compare U. R. Evans, *J. Soc. Chem. Ind.*, 1925, **44**, 163T). There was also some velvety black deposit on the back where the electrode touched the glass. Black cupric oxide had collected as a loose precipitate on the bottom of the trough, whilst a very adherent black layer had been produced on the glass on each side of the electrode at the water level. The liquid was found, after filtration, to contain copper. Apparently at the water line the copper had passed into solution as sodium cuprate, which hydrolysed, yielding cupric oxide, partly in the liquid, partly on the surface of the glass, and to some extent on the copper also. Electrolysis at 1 m.a./sq.cm. yielded similar results.

At 0·25 m.a./sq.cm. the behaviour was quite different. No oxygen bubbles appeared on the anode, which began to turn brown within 6 minutes; after an hour it was wholly covered with a velvety black deposit. At the end of 5 hours, the anode was taken out and dried. The velvety deposit had a matt sooty character, the lustre of the copper being lost; the appearance suggested that the sooty deposit was a secondary product—not due to direct oxidation. Very possibly—when the current density is insufficient to produce

passivity—the copper suffers anodic attack, yielding sodium cuprate, which (in the absence of the stirring due to oxygen evolution) decomposes in contact with the copper itself, yielding the velvety black deposit of oxide. An experiment at 0·1 m.a./sq.cm. gave a similar result.

Several experiments were performed also with mechanically stirred electrolyte. An experiment at 0·1 m.a./sq.cm. produced colours on the anode as well as on the cathode. The colours on the anode appeared in the same sequence as those on the cathode, and in the well-stirred solution were quite brilliant. It seems quite possible that even these brightly coloured anodic oxide films may be produced by decomposition of cuprate.

Blank specimens to which no external current was applied showed no change in the time ($\frac{1}{2}$ to 2 hours) required to produce advanced colours on cathode and anode. But copper strips half-immersed in N/10-sodium hydroxide for one night showed the familiar "differential aeration phenomena." The upper (cathodic) part to which oxygen had best access merely acquired a brown tarnish, whilst the lower (anodic) portion became covered with a black matt deposit; there were narrow black lines along the water level.

The Effect of an Invisible Oxide Film on the Chemical Behaviour of Copper.—Further information on this point was obtained by means of silver nitrate—a plan suggested by the work of Dunstan and Hill (J., 1911, **99**, 1853) and that of Bengough and Hudson (*J. Inst. Metals*, 1919, **21**, 107). Copper exposed to dry air for 17 hours was darkened by N/25-silver nitrate much less quickly than freshly ground copper; exposure to carbon dioxide had no such effect, which must be attributed, therefore, to oxidation, not to self-annealing.

A strip of copper was held in pliers at one end and the other end brought over the flame of a burner, so as to give the ordinary sequence of colours. After cooling in a desiccator, an area at the unheated end was again ground with emery, and the whole length of the strip was dipped under N/25-silver nitrate. The freshly ground portion blackened immediately, whilst at the other end the area covered by very thick scale began to develop glittering crystals of silver within 10 seconds, probably owing to cracks in the scale. But after 35 seconds the area covered by the first-order tints, and also the region adjacent to the first-order brown upon which no tint was visible, were practically unchanged apart from a very few, tiny crystals of silver. The protective action of the invisible film was here very clearly marked.

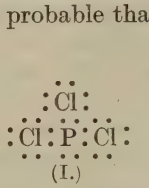
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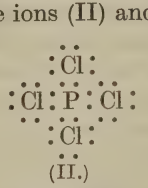
[*Received, August 17th*, 1925.]

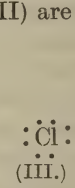
CCCXLI.—*The Electrical Conductivity of Phosphorus Pentachloride.*

By GEORGE WILLIAM FRASER HOLROYD, HARRY CHADWICK, and JOSEPH ERNEST HALSTEAD MITCHELL.

ABOUT 2 years ago, one of us (G. W. F. H., *Chem. and Ind.*, 1923, 348) suggested that when phosphorus trichloride (I) combines with chlorine it is probable that the ions (II) and (III) are produced.


(I.)


(II.)


(III.)

In this connexion, using a cell with a constant of about 0·6 and applying an *E.M.F.* of 6 volts, we found that a saturated solution of phosphorus pentachloride in nitrobenzene gave a current of 0·009 amp., a 1·5% solution of hydrogen chloride in nitrobenzene gave 0·0007 amp., phosphorus trichloride introduced into nitrobenzene with no special precautions to exclude moisture gave a just perceptible current, whilst the following gave no current: (1) nitrobenzene; (2) solutions of phosphorus pentachloride in (*a*) ethylene dibromide, (*b*) benzene, (*c*) phosphorus trichloride; (3) hydrogen chloride in ethylene dibromide; (4) hydrogen chloride in phosphorus trichloride.

Plotnikov (*Z. physikal. Chem.*, 1907, **48**, 220) observed that phosphorus pentabromide dissolved in bromine conducted the current, but he states (*Chem. and Ind.*, 1923, 750) that phosphorus is formed at the cathode and combines with the bromine to form pentabromide.

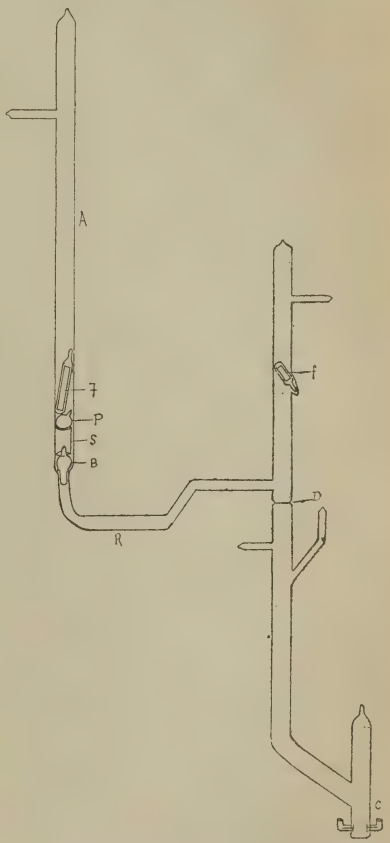
We propose to examine the nature of the ions formed in the case of the pentachloride, and to examine the solution of this substance in nitrobenzene in other respects, and desire to reserve this field of investigation for the present.

EXPERIMENTAL.

The chlorides of phosphorus were prepared in the following manner. Yellow phosphorus was melted in a stout tube, and water which rose to the surface was removed with filter-paper. The phosphorus was sucked up into a glass syringe, where it was allowed to solidify. The narrow nozzle of the syringe was passed through a rubber stopper into a tube from which dry nitrogen was issuing. Into this tube the phosphorus was discharged. From

this tube the phosphorus was distilled in dry atmospheric nitrogen into a receiver. From the latter the phosphorus was run into a second tube, which was then sealed off from the receiver, and from which the phosphorus was again distilled in dry atmospheric nitrogen and collected in bulbs holding 0·5 to 5 g. of phosphorus. These bulbs were then sealed off, cleaned, and introduced into the tube A (see Fig.). The latter was sealed off, filled with dry nitrogen, and the bulb was broken with the help of a magnet acting on F.

Fig. 1.



P, bulb of phosphorus; F, iron rod sealed up in glass tube; S, frail glass support; B, bulb with spiked top; D, diaphragm; C, conductivity cell; R, reaction chamber; f, similar to F.

Chlorine, prepared from dichromate and hydrochloric acid through which hydrogen chloride had been passed to expel air, was washed and dried and passed over the phosphorus in such quantity as to form the trichloride or the pentachloride. In the latter case, excess chlorine was expelled by dry nitrogen. The inlet and outlet tubes were then sealed, and the cell below the diaphragm was filled with nitrogen and sealed.

For solutions of phosphorus pentachloride in nitrobenzene, the latter was introduced into the cell before sealing. Communication between the tube A and the cell was then made by breaking the diaphragm.

The phosphorus had a great tendency to remain liquid after being sealed up in the bulbs, remaining liquid in one bulb for more than 6 months.

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Blackburn.

[*Received, August 26th,* 1925.]

CCCXLII.—*The Occurrence of Sylvestrene.*

By B. Sanjiva Rao and John Lionel Simonsen.

It has been shown in previous communications (J., 1920, **117**, 571; 1922, **121**, 2294; *Ind. For. Rec.*, 1924, **10**, 161) that it is a characteristic property of *d*-Δ^3-carene and *d*-Δ^4-carene to yield on treatment with hydrogen chloride a mixture of sylvestrene dihydrochloride and dipentene dihydrochloride, the dicyclic system being disrupted by fission of the *cyclo*propane ring. To students of terpene chemistry the occurrence in nature of the hydrocarbon sylvestrene has always appeared to be somewhat anomalous, because it is the only naturally occurring terpene derived from *m*-cymene, all the other members of the group being *p*-cymene derivatives.

Although sylvestrene has been reported present in a considerable number of oils (" Organische Chemie," Beilstein, 4th ed., V, 125), it occurred to us that the hydrocarbon may not actually exist as such in nature, but that it may arise during the process of isolation and purification. A careful survey of the somewhat extensive literature appeared to us to offer sufficient support for this hypothesis to warrant its further investigation.

Sylvestrene was first isolated by Atterberg (*Ber.*, 1877, **10**, 1023) from Swedish pine-tar oil derived from *Pinus sylvestris*, and its constitution was subsequently established by the investigations of Wallach (*Annalen*, 1885, **230**, 240; 1887, **239**, 24), of Baeyer (*Ber.*, 1894, **27**, 1915; 1898, **31**, 2067), and of Perkin and his collaborators (J., 1907, **91**, 482; 1908, **93**, 1888; 1913, **103**, 2229). For the identification of the hydrocarbon, Atterberg (*loc. cit.*, p. 1208) treated the appropriate fraction of the oil with hydrogen chloride, when sylvestrene dihydrochloride, m. p. 72°, was readily obtained. This method appears to have been adopted by all subsequent investigators. It is not without significance that Atterberg (*loc. cit.*, p. 1208) in one experiment could obtain only a dihydrochloride, m. p. 50° (the melting point of dipentene dihydrochloride), since it has been shown that in some cases *d*-Δ^4-carene on treatment with hydrogen chloride yields dipentene dihydrochloride in larger quantity than sylvestrene dihydrochloride and the former therefore crystallises on cooling. Reference to the formation of dipentene dihydrochloride during the purification of sylvestrene is also made by Bertram and Wahlbaum (*Arch. Pharm.*, 1893, **231**, 301), who separated the latter only by prolonged fractional crystallisation and were unable to establish the presence of dipentene in the original oil by the direct preparation of its derivatives.

Perhaps the most characteristic property of sylvestrene, a reaction

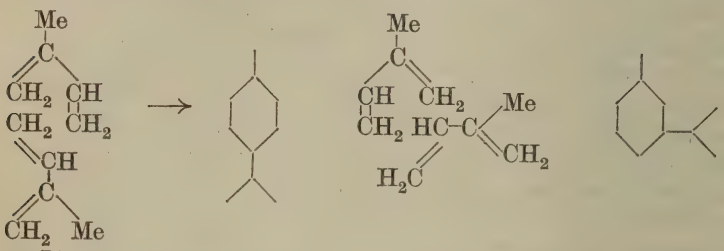
not shown by any other monocyclic terpene, is the deep blue colour developed by an acetic anhydride solution of the hydrocarbon when treated with a drop of concentrated sulphuric acid. The absence of this reaction in the case of the crude terpene separated from the oil of *P. sylvestris* was observed by Wallach, but in spite of this he was inclined to regard the presence of the terpene in the original oil as being established. Bertram and Wahlbaum (*loc. cit.*, p. 299), working with Swedish pine-needle oil from *P. sylvestris*, obtained a faint violet coloration, and a similar observation was made by Umney (*Pharm. J.*, 1895, **55**, 167), working with Scotch pine-needle oil. Mörner (*Svensk Farm. Tids.*, 1909, 317), in a paper which does not appear to have been abstracted, has made a full and careful investigation of the colour reactions of the various fractions of the oil from *P. sylvestris*. He found that all fractions of the oil boiling below 185° gave a transient violet coloration, and that an indigo-blue colour was given only by the sesquiterpene fraction, which is known to contain cadinene. He specifically mentions that the blue colour shown by certain samples of the *whole* oil from *P. sylvestris* needles cannot be due to the presence of sylvestrene. In a later communication (*ibid.*, p. 1913), he established the same facts in the case of the oils derived from *P. sylvestris*, *P. pumilio*, and *P. abies* of varying origins. The evidence, therefore, appeared to be against the existence of sylvestrene in these oils, and it is significant that a transient purple or violet coloration is characteristic of carene.

We have submitted the oil from *P. sylvestris* to a very careful examination. The oil used by us was obtained from A. Carlsson's Enkas Tallbarrolye Fabrik, Jönköping, Sweden, and was of undoubted authenticity. We have been quite unable to find any trace of sylvestrene in the oil, although we have found it to contain *d*-Δ^3-carene in considerable quantity.

This hydrocarbon was identified by the preparation of the characteristic nitrosate (decomposing at 147·5°) and also by the formation of sylvestrene dihydrochloride, m. p. 72°. *d*-Δ^3-Carene was found to be present in all the fractions of the oil boiling below 180° (more than 70% of the total distillate), except in that distilling at 153—157°/684 mm. (see p. 2497). From the sesquiterpene fraction (b. p. 185—187°/100 mm.) *l*-cadinene was separated as the dihydrochloride, and this fraction of the oil gives the well-known colour reactions associated with this sesquiterpene. We consider ourselves justified in stating that the oil from *P. sylvestris* of Swedish origin contains *d*-Δ^3-carene and does not contain *d*-sylvestrene, the previous isolation of *d*-sylvestrene from the oil being due to the decomposition of the dicyclic terpene.

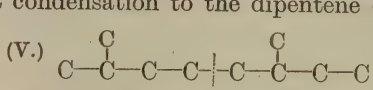
We have also examined a small sample of the oil from *P. pumilio*, of unknown origin, obtained by purchase from Messrs. Boake, Roberts and Co. The oil was considerably resinified and therefore had a high density; like the oil from *P. sylvestris*, it was found to be free from sylvestrene whilst containing Δ^3-carene. This terpene thus appears to occur somewhat frequently in nature, and in view of its ready identification by means of the sparingly soluble nitrosate, its detection presents little difficulty.*

The probable absence of sylvestrene from natural terpenes is not without theoretical importance. If, as is generally assumed, the terpenes and sesquiterpenes arise from polymerisation of two or more molecules of isoprene, the occurrence of sylvestrene would offer no difficulty (I, II, III, and IV).



(I.) (II.) (III.) (IV.)

Recently, however, Ingold (*Annual Reports*, 1924, **21**, 102) has suggested that the geraniol chain (V) may more correctly be regarded as the first stage in the union of two isoprene molecules, with subsequent condensation to the dipentene (*p*-cymene) type (II).



(V.) (II.)

This proposal, owing to its simplification of sesquiterpene chemistry, has obviously much to recommend it; but it would clearly be inapplicable if sylvestrene occurred in nature. The proof offered in this note of the absence of sylvestrene in the oils from *P. sylvestris* and *P. pumilio* makes it improbable that this terpene occurs in other oils and thus lends support to Ingold's suggestion.

We wish to take this opportunity of expressing our thanks to Professor V. Henriques of the University of Copenhagen for obtaining for us the sample of the oil from *P. sylvestris*, without

* Aschan (A., 1919, i, 336) has stated that during an investigation of Finnish turpentine he succeeded in isolating a new hydrocarbon, b. p. 163—165°, which, since it yielded pinene nitrosochloride, was closely related to α-pinene. We have been able to consult this paper in abstract only, but we venture to suggest that in all probability he was dealing with a mixture of α-pinene and Δ^3-carene, which are very difficult to separate.

which it would not have been possible for us to undertake this investigation.

Experimental.

Section I. The Oil from Pinus sylvestris.

The oil used in these experiments was pale yellow in colour and after drying over anhydrous magnesium sulphate had the following constants: $d^{30°}_{30°}$ 0·8661, $n^{30°}_{D}$ 1·4729, $[\alpha]^{30°}_{D}$ + 13·2°, acid value 0·28, saponification value 6·7, saponification value after acetylation 15·0.

A quantity of the oil was subjected to a prolonged systematic fractionation using a four-pear Young still-head, the distillation being carried out at first under diminished pressure and finally at the ordinary pressure, when the following fractions were obtained:

Table I.

No.	B.p. (684 mm.).	$d^{30°}_{30°}$.	$n^{30°}_{D}$.	$[\alpha]^{30°}_{D}$.	Yield % of original oil.
i	153—157°	0·8553	1·4637	+20·0°	17·4
ii	157—161	0·8553	1·4656	+16·7	18·7
iii	161—167	0·8556	1·4676	+11·7	30·0
iv	167—176	0·8573	1·4711	+ 8·0	8·1

Fraction (*i*). This fraction consisted of nearly pure α-pinene, the presence of this hydrocarbon being established by the preparation of the nitrosochloride decomposing at 107° and the nitrolpiperide, m. p. 118—119°.

Fraction (*ii*). This fraction consisted of a mixture of α-pinene, β-pinene, and *d*-Δ^3-carene. The presence of α-pinene was proved by the preparation of the derivatives mentioned above and by oxidation to pinonic acid (semicarbazone decomposing at 207°); β-pinene was shown to be present in very small amount by oxidation to nopinic acid, identified by the method of mixed melting points. The presence of *d*-Δ^3-carene was established by the preparation of the nitrosate, which, after recrystallisation, decomposed at 147·5° and was found to be identical in every way with a specimen of the nitrosate from another source. On treatment of a portion of the oil with hydrogen chloride, *d*-sylvestrene dihydrochloride was obtained which melted at 72°, and this m. p. was unaltered on admixture with a specimen of the *d*-dihydrochloride from another source.

Fraction (*iii*). This fraction consisted essentially of *d*-Δ^3-carene (nitrosate, decomp. 147·5°; *d*-sylvestrene dihydrochloride, m. p. 72°). When oxidised in acetone solution with potassium permanganate, only a very small trace of a keto-acid was formed, and this was identified as pinonic acid. No indication was obtained of the presence of either Δ^4-carene or β-pinene. When dissolved in chloroform and treated with a chloroform solution of bromine, one molecule of bromine was absorbed, the fairly sharp end-point

indicating the probable absence of any but dicyclic terpenes in this fraction of the oil. When dissolved in acetic anhydride and treated with a drop of concentrated sulphuric acid, a transient purple coloration was observed.

Fraction (iv). This fraction consisted of nearly pure *d*-Δ^3-carene.

During the distillation of the oil a considerable fraction was obtained which distilled above 115°/100 mm.; after treatment with alcoholic potassium hydroxide solution to hydrolyse any esters present, the residual oil was carefully fractionated, when two main fractions were obtained: (*a*) b. p. 167—173°/683 mm., which was identified as *d*-Δ^3-carene ($d_{30°}^{30°}$ 0·8573, $n_D^{30°}$ 1·471; nitrosate, decomp. 147·5°), and (*b*) a viscid, yellow oil, b. p. 185—187°/100 mm. This after distillation over sodium had the constants $d_{30°}^{30°}$ 0·9082, $n_D^{30°}$ 1·499, $[\alpha]_D^{30°}$ + 24·0°. When it was dissolved in acetic anhydride and treated with a drop of concentrated sulphuric acid, an emerald-green colour was obtained which changed to deep indigo-blue. This colour reaction was due to the presence of *l*-cadinene, the presence of which was established by the preparation of the dihydrochloride, m. p. 118°; and this m. p. was not depressed on admixture with an authentic specimen. In chloroform solution (5%), $[\alpha]_D^{30°} = -38·1°$, which is in good agreement with the value found by Wallach ($[\alpha]_D$ — 36·8°) (*Annalen*, 1899, **252**, 150) for this substance.

Section II. The Oil from Pinus pumilio.

The oil, of which only slightly more than 100 g. were available for examination, was dried over anhydrous magnesium sulphate and the constants were determined: $d_{30°}^{30°}$ 0·9221, $n_D^{30°}$ 1·4831, $[\alpha]_D^{30°}$ — 9·3°, acid value 7·5, saponification value 31·5, saponification value after acetylation 89·6. The density of the oil was considerably higher than had been previously observed for samples of this oil, a fact probably due to the oil containing a large quantity of resinous material, which remained behind in the distilling flask on fractionation.

After the separation of the portion distilling above 140°/100 mm., the oil * was fractionated at the ordinary pressure, when the following fractions were obtained:—

TABLE II.

No.	B.p. (685 mm.).	$d_{30°}^{30°}$.	$n_D^{30°}$.	$[\alpha]_D^{30°}$.	Yield % of the original oil.
i	155—160°	0·8512	1·4648	—12·6°	16·5
ii	160—163	0·8529	1·4675	—14·7	14·3
iii	163—166	0·853	1·4691	—15·7	7·0
iv	166—175	0·8561	1·4711	—21·3	8·0

* Prior to distillation, the oil was treated with an alcoholic solution of potassium hydroxide to remove the free acids and to hydrolyse any esters.

An examination of these fractions has shown *fraction* (*i*) to consist essentially of α-pinene (nitrosochloride, decomp. 107°; nitrolpiperide, m. p. 118—119°); Δ^3-carene was absent, since no crystalline nitrosate was obtained. *Fractions* (*ii*) and (*iii*) contained α-pinene and Δ^3-carene,* since both fractions gave a nitrosochloride (decomp. 107°) and a nitrosate (decomp. 147·5°). Owing to the small quantity of material available, no attempt was made to examine these fractions for β-pinene, the presence of this hydrocarbon in the oil from *P. pumilio* having been established by previous workers.

Fraction (*iv*) consisted mainly of Δ^3-carene, an excellent yield of the nitrosate being obtained. When it was dissolved in acetic anhydride and treated with a drop of concentrated sulphuric acid, a transient purple coloration was observed, but the blue coloration characteristic of sylvestrene could not be obtained.

The higher-boiling fractions of the oil were not examined.

INDIAN INSTITUTE OF SCIENCE,
BANGALORE.

[*Received, September 14th*, 1925.]

CCCXLIII.—*The Colorimetric Dissociation Constants of 3 : 5-Dinitrocatechol and 4 : 6-Dinitroresorcinol.*

By FRANK CHARLES LAXTON, EDMUND BRYDGES RUDHALL PRIDEAUX, and WILLIAM HOWARD RADFORD.

THE investigation of the colorimetric dissociation constants of the nitroquinols (Prideaux and Nunn, J., 1924, **125**, 2110) has now been extended to include 3 : 5-dinitrocatechol and 4 : 6-dinitroresorcinol. These compounds show fewer colour changes than the nitroquinols, and therefore give fewer colorimetric constants. Substantially the same methods of colour matching and determination of p_H were used, *viz.*, (i) the drop method, with alkaline 2 : 4-dinitrophenol as standard for the amount of substance transformed, (ii) the drop method with completely transformed indicator as standard (*loc. cit.*, p. 2113), (iii) the method in which, by the addition of N drops of indicator, the colour of the solution is made to match that of a combination of an alkaline solution of the dinitrophenol containing x drops of the indicator and an acid solution containing $N—x$ drops (*loc. cit.*) :

$$p_k = p_H + \log \{(N - x)/x\}.$$

* It was not determined if Δ^3-carene was present in the dextro- or lævorotatory form.

3 : 5-*Dinitrocatechol.*—This compound was obtained in yellow, hexagonal plates, m. p. 164°, by Nietzki and Moll's method (*Ber.*, 1893, **26**, 2183).

Colorimetric Constants.—The colour changes were investigated by means of a British Drug Houses comparator and a set of solutions ranging in p_H from 4·22 to 12·05. Each tube contained 10 c.c. of buffer solution and 5 drops of an $M/20$-solution of the indicator. Dinitrocatechol was colourless in acid solutions. The full yellow colour occurred at p_H 5·34 and was constant up to p_H 7·6. The orange colour, obviously transitional, was not constant over any appreciable range of p_H and so was not investigated. The complete reddish-brown stage occurred at p_H 12·05 and was unchanged by the addition of $N/5$-alkali. In presence of very strong alkali ($6N$-potassium hydroxide), this indicator developed a purple colour.

As dinitrocatechol, owing to its orange-yellow colour, could not be matched against dinitrophenol, p_{k_1} and p_{k_2} were determined by method (iii); the tube containing the acid solution, which was colourless, was omitted in each case. Four tubes were prepared containing 10 c.c. of buffer solution of p_H 3·1, 3·337, 3·674, and 3·911, respectively. A match was obtained under the following conditions :

p_H of solution.		Full yellow. (above 5·34)	3·1	3·337	3·674	3·911
Drops of $M/20$-D.N.C.	*a*	8	18	14	11	10
	b	12	28	21	17	15
p_{k_1}	*a*	3·20	3·21	3·25	3·31	
	b	3·22	3·21	3·29	3·31	
Mean		3·21	3·21	3·27	3·31	Grand mean 3·25.

The halfway change is obviously between p_H 3·1 and 3·337.

Determination of p_{k_2}.—*Halfway change.* A yellow solution in which the first change was complete (p_H 6·47), containing 5 drops of the indicator, placed behind a reddish-brown alkaline solution (p_H above 12·05) containing 5 drops of the indicator, matched a solution of p_H 10·39 containing 10 drops of indicator.

$$p_{k_2} = p_H + \log (N - x)/x = 10{\cdot}39 + \log 5/5 = 10{\cdot}39.$$

Quarterway change. A yellow solution of p_H 6·47 containing 9 drops of indicator placed behind an alkaline solution containing 3 drops of indicator, matched a solution of p_H 9·83 containing 12 drops of indicator.

$$p_{k_2} = p_H + \log (N - x)/x = 9{\cdot}83 + \log 9/3 = 10{\cdot}31.$$

2-*Nitroresorcinol.*—This compound was made by Kauffmann and Pay's method (*Ber.*, 1904, **37**, 725).

Solutions were prepared as in the case of dinitrocatechol ranging in p_H from 4·22 to 12·05, and tested with an $M/20$-alcoholic solution

of the nitroresorcinol. Even in acid solution the indicator showed a pure yellow colour, and therefore it was not possible to determine p_{k_1}, which must have been very low.

The colour, the first darkening of which was noticed at p_H 5·34, became a full reddish-brown at p_H 7·6 and faded to a pale dull brown at a higher p_H. The colours in all cases were less intense than those given by dinitrocatechol in a solution of the same strength.

Determination of p_{k_2}.—*Halfway change to reddish-brown.* An acid solution containing 8 drops of the indicator, placed behind the reddish-brown solution (p_H 7·6) containing 8 drops of the indicator, matched a solution (p_H 6·47) containing 16 drops of the indicator.

$$p_{k_2} = p_H + \log (N - x)/x = 6{\cdot}47 + \log 8/8 = 6{\cdot}47.$$

Quarterway change. An acid solution containing 12 drops of the indicator, placed behind a reddish-brown solution (p_H 7·6) containing 4 drops of the indicator, matched a solution (p_H 5·68) containing 16 drops of the indicator.

$$p_{k_2} = p_H + \log (N - x)/x = 5{\cdot}68 + \log 12/4 = 6{\cdot}16.$$

Three-quarterway change. An acid solution containing 2 drops of the indicator, placed behind a reddish-brown solution (p_H 7·6) containing 6 drops of the indicator, matched a solution (p_H 6·87) containing 8 drops of the indicator.

$$p_{k_2} = p_H + \log (N - x)/x = 6{\cdot}87 + \log 2/6 = 6{\cdot}39.$$

The mean value for p_{k_2} is 6·34; hence k_2 for the second change is $4{\cdot}57 \times 10^{-7}$.

4 : 6-*Dinitroresorcinol.*—This compound was obtained in yellow prisms, m. p. 214·5°, by Typke's method (*Ber.*, 1883, **16**, 552). It is only sparingly soluble in water or alcohol. A saturated alcoholic solution was used containing 0·12 g. per 100 c.c. As in the former cases, a set of solutions was prepared of various p_H values and tested with the indicator.

Solutions of p_H less than 3·1 were colourless; for higher values, the colour was yellow and deepened up to p_H 6·47; there was no further change after the full yellow colour had developed.

The halfway change to the yellow was found as in the two previous cases: $p_{k_1} = 4{\cdot}22$.

The apparent strengths of the substances as deduced from their colorimetric constants (p_{k_1}) are: 2-nitroresorcinol, very low; 2 : 5-dinitroquinol, 2·8; mononitroquinol, 3·25; 3 : 5-dinitrocatechol, 3·25; 4 : 6-dinitroresorcinol, 4·22, *i.e.* the strengths diminish in the order given.

UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, July 29th,* 1925.]

CCCXLIV.—*Symmetrical Substitution Derivatives of Trimethylene Dibromide and Pentamethylene Dibromide.*

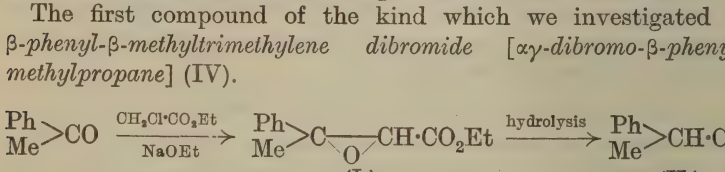
By William Hobson Mills and Leslie Bains.

Symmetrically substituted trimethylene or pentamethylene dibromides of the types $CH_2Br{\cdot}CRR'{\cdot}CH_2Br$ and

$$CH_2Br{\cdot}CH_2{\cdot}CRR'{\cdot}CH_2{\cdot}CH_2Br$$

(where R may be a hydrogen atom) would be of value for the synthesis of several compounds of stereochemical interest, but such dihalides have not hitherto been described. We have therefore undertaken the preparation of representatives of each class.

The first compound of the kind which we investigated was *β-phenyl-β-methyltrimethylene dibromide* [*αγ-dibromo-β-phenyl-β-methylpropane*] (IV).



The starting point for this preparation was hydratropaldehyde (II), which is readily obtained by the method of Darzens (*Compt. rend.*, 1904, **139**, 1214; compare Claisen, *Ber.*, 1905, **38**, 703) from acetophenone through ethyl β-phenyl-β-methylglycidate (I). We found that, like other disubstituted acetaldehydes (Apel and Tollens, *Ber.*, 1894, **27**, 1087; Just, *Monatsh.*, 1896, **17**, 76; compare Neustädter, *Annalen*, 1907, **351**, 294), hydratropaldehyde reacts with formaldehyde and alkali to give a *glycol*. In this case, however, the reaction takes place with great readiness and, although potassium carbonate was used as a condensing agent instead of a caustic alkali, the glycol was obtained directly, and no trace of an aldol, which presumably forms an intermediate stage in the reaction, could be detected (compare Wessely, *Monatsh.*, 1900, **21**, 216). The conversion of the glycol into the dibromide, however, presented considerable difficulty. It was finally effected through the prolonged action of hydrogen bromide on the *glycol diacetate* (see Perkin and Simonsen, J., 1905, **87**, 855).

Suspecting that this difficulty was connected with the presence in the molecule of two substituents, phenyl and methyl, on the same carbon atom, we prepared the simpler compound, β-*phenyl-*

trimethylene dibromide [*αγ-dibromo-β-phenylpropane*] (VI), by the action of hydrogen bromide on the diacetate of the glycol (V),

$$CHPh{:}CH_2 \xrightarrow[H_2SO_4,HA]{CH_2O} \underset{(V.)}{CHPh(CH_2{\cdot}OH)_2} \longrightarrow \underset{(VI.)}{CHPh(CH_2Br)_2}$$

which was prepared as described by Prins (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 21) by the action of trioxymethylene, acetic acid, and sulphuric acid on styrene. This diacetate reacted with hydrogen bromide much more readily than that of phenylmethyltrimethylene glycol, and under suitable conditions gave 70%, or more, of the theoretical yield of dibromide.

A γ-substituted pentamethylene dibromide could, we found, be obtained with comparative readiness from the di-β-phenoxyethylacetic acid (VII) described by Bentley, Haworth, and Perkin (J.,

(VII.) $PhO{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CH_2{\cdot}OPh \longrightarrow$
$CH_2Br{\cdot}CH_2{\cdot}CH(CO_2Et){\cdot}CH_2{\cdot}CH_2Br$ (VIII.)

1896, **69**, 169). The phenoxy-groups were replaced by bromine by heating with concentrated hydrobromic acid and the resulting dibromo-acid was converted into *γ-carbethoxypentamethylene dibromide* [*ethyl αε-dibromopentane-γ-carboxylate*] (VIII) by treatment with alcoholic hydrogen bromide.

This compound proved more reactive than the substituted trimethylene dibromides, and to investigate its applicability to syntheses we studied its behaviour towards piperidine. The two substances reacted smoothly, giving a compound which from its composition, method of formation and reactions could only be the *spirocyclic* ammonium salt, 4-*carbethoxybispiperidinium*-1 : 1′-*spiran bromide* (IX). The corresponding reaction between piperidine and pentamethylene dibromide was described by von Braun (*Ber.*, 1906, **39**, 4351).

$$2CH_2\!<\!\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}\!>\!NH + \begin{matrix}CH_2Br{\cdot}CH_2\\CH_2Br{\cdot}CH_2\end{matrix}\!>\!CH{\cdot}CO_2Et$$
$$= \Big[CH_2\!<\!\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}\!>\!N\!<\!\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}\!>\!CH{\cdot}CO_2Et\Big]Br + C_5H_{11}N,HBr.$$
(IX.)

It is proposed to make further applications of these compounds.

Experimental.

β-Phenyl-β-methylpropane-αγ-diol (III).—A mixture of hydratropaldehyde (55 g.), formalin (98 c.c. of 38% formalin diluted with 80 c.c. of water), and potassium carbonate (30 g.) was stirred vigorously at 100° for 13 hours. In subsequent preparations

sufficient alcohol was added to give a homogeneous mixture when hot; this enabled the stirring to be dispensed with. Unchanged aldehyde and alcohol were removed by distillation with steam. The insoluble product left was taken up in boiling benzene, the benzene evaporated, and the residue distilled. The portion boiling at 180—210°/15 mm. was nearly pure *glycol* and solidified in fan-shaped clusters of silky needles. Crystallised from benzene, the glycol forms needles, m. p. 88°, b. p. 184°/17 mm., having a bitter taste which develops tardily (Found : C, 72·1; H, 8·5. $C_{10}H_{14}O_2$ requires C, 72·2; H, 8·5%). It is very soluble in alcohol, commercial ether, or chloroform. It is less soluble in anhydrous ether and is sparingly soluble in benzene.

The *diacetate*, $CPhMe(CH_2{\cdot}O{\cdot}CO{\cdot}CH_3)_2$, was prepared by gently boiling the glycol for 7 hours with acetic anhydride (2½ parts) and anhydrous sodium acetate (1 part). The product was isolated by pouring into water, extracting with ether, and distilling under diminished pressure. It formed a colourless liquid, b. p. 179°/20 mm. (Found : C, 67·1; H, 7·3. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·3%) : Yield 88—91% of the theoretical.

αγ-Dibromo-β-phenyl-β-methylpropane (IV).—The diacetate was dissolved in glacial acetic acid saturated with hydrogen bromide at 0° (6 parts) and heated for 30 hours at 100°. After pouring into water, extracting with ether, washing with sodium carbonate, and removing the ether, a dark oil (150 g. from 200 g. of the diacetate) was obtained. As examination of this after distillation in a vacuum showed that bromination was not nearly complete, the treatment with hydrogen bromide in acetic acid solution was repeated. The oil (65 g.) gave a product from which, by fractionally distilling three times, a fraction (20·5 g.), b. p. 143—146°/12 mm., was obtained. This was the pure *dibromide* (Found : C, 41·4; H, 4·3; Br, 54·55. $C_{10}H_{12}Br$ requires C, 41·1; H, 4·2; Br, 54·7%). It has a powerful geranium-like odour.

α-Bromo-γ-hydroxy-β-phenyl-β-methylpropane, $CH_2Br{\cdot}CPhMe{\cdot}CH_2{\cdot}OH$.—A solution of the glycol (9 g.) in the minimum of glacial acetic acid was saturated at 0° with hydrogen bromide during 3 hours and then heated at 100° while a slow stream of the gas was passed through it for 7 hours. After keeping over-night, the product was isolated by pouring into water, extracting with ether, and fractional distillation. The fraction b. p. 173°/15 mm. contained the percentage of bromine required for the *bromohydrin* (Found : Br, 34·6. $C_{10}H_{13}OBr$ requires Br, 34·9%).

α-Chloro-γ-hydroxy-β-phenyl-β-methylpropane, $CH_2Cl{\cdot}CPhMe{\cdot}CH_2{\cdot}OH$.

—The glycol (10 g.) was added to phosphorus pentachloride (26 g.), and the mixture kept at 80° for 2 hours. Water was then added, and the product isolated by distilling with steam, extracting the distillate with ether, and fractionation under diminished pressure. A colourless liquid (2·5 g.), b. p. 118—121°/15 mm., containing 19·6% of chlorine was thus obtained.

Another method of preparation was also tried. The glycol (10 g.) was dissolved in pyridine (9·6 g.), and thionyl chloride (15 g.) added during 20 minutes. After keeping over-night, the mixture was heated at 105° for 1½ hours and the product was then isolated as in the foregoing experiment. A colourless liquid (2·8 g.), b. p. 122°/19 mm., containing 19·6% of chlorine was obtained. The products of the two experiments were united and by refractionation a liquid which was regarded as the chlorohydrin was obtained, b. p. 117—118°/15 mm. (Found: Cl, 19·2. $C_{10}H_{13}OCl$ requires Cl, 19·3%).

α-*Bromo*-γ-*acetoxy*-β-*phenyl*-β-*methylpropane*, $CH_2Br{\cdot}CPhMe{\cdot}CH_2{\cdot}OAc$.—The diacetate (30 g.) was dissolved in an equal volume of glacial acetic acid, and hydrogen bromide was led in at 90—95° for 10 hours after the mixture had become saturated. The product isolated by pouring into water, ether extraction, and distillation contained only 15% of bromine. The treatment with hydrogen bromide was therefore repeated and allowed to proceed for 19 hours. The product now distilled at 174—174·5°/18 mm. and was the pure bromoacetate (Found: C, 53·2; H, 5·7; Br, 29·5. $C_{12}H_{15}O_2Br$ requires C, 53·1; H, 5·6; Br, 29·5%).

α*γ*-*Dibromo*-β-*phenylpropane* (VI).—αγ-Diacetoxy-β-phenylpropane (17·4 g.) (Prins, *loc. cit.*) was saturated with hydrogen bromide in the cold and then kept at 90° for 15 hours whilst a slow stream of the gas was led through. The product, which had absorbed rather more than the theoretical weight of the gas, was poured into water, and the *dibromide* isolated by extraction with ether and distillation. Practically the whole (14·4 g.) boiled at 152°/14 mm. and proved to be the pure dibromide (Found: C, 39·5; H, 3·6; Br, 57·4. $C_9H_{10}Br_2$ requires C, 39·8; H, 3·6; Br, 57·5%). The compound has a strong geranium-like odour.

Ethyl αε-*Dibromopentane*-γ-*carboxylate* (VIII).—Di-β-phenoxyethylacetic acid (Bentley, Haworth, and Perkin, *loc. cit.*) (30 g.) was boiled for 10—12 hours with a mixture of constant-boiling hydrobromic acid (150 c.c.) and fuming hydrobromic acid (50 c.c.). The resulting mixture of di-β-bromoethylacetic acid and phenol, after separation from the hydrobromic acid by dilution with water and extraction with ether, was dissolved in alcohol, and the solution

saturated with hydrogen bromide (3 days) and then kept for a week. The product was isolated by addition of water, extraction with ether (the phenol being removed by shaking the ethereal solution with dilute aqueous sodium hydroxide) and distillation under diminished pressure. The *dibromo-ester* was a heavy oil with a garlic-like odour, b. p. 166—167°/19 mm. (Found: C, 32·3; H, 4·6; Br, 52·9. $C_8H_{14}O_2Br_2$ requires C, 31·8; H, 4·7; Br, 52·9%).

4-*Carbethoxybispiperidinium*-1 : 1′-*spiran Picrate* (formula corresponding with IX).—Ethyl αε-dibromopentane-γ-carboxylate (17 g.) and piperidine (10·6 g.) were dissolved in alcohol (350 c.c.) and the mixture was boiled for 48 hours. After evaporation of the alcohol and digestion with ether, the residue was treated with an aqueous solution of potassium hydroxide (1 equiv.), and the piperidine set free was removed by extraction with ether. The water was then completely removed by evaporation under diminished pressure and the spiro*ammonium bromide* was separated from the potassium bromide by extraction with *anhydrous* chloroform. Evaporation of the chloroform left it as a faintly yellow oil (12·3 g.), which rapidly solidified and could be recrystallised from alcohol and ether, but was exceedingly hygroscopic. The crude bromide (12·3 g.) was therefore converted into the *picrate* by treatment with a solution of picric acid (9·2 g.) in a mixture of alcohol (100 c.c.) and water (160 c.c.). The picrate, recrystallised from alcohol, formed large, golden-yellow, rhombic prisms (7 g.), m. p. 130° (Found: N, 12·1. $C_{19}H_{26}O_9N_4$ requires N, 12·3%).

4-*Carboxybispiperidinium*-1 : 1′-*spiran Bromide*.—The carbethoxy-group in the above compound (5·8 g.) was hydrolysed to carboxyl by boiling with dilute hydrobromic acid (250 c.c. of water and 30 c.c. of constant-boiling acid) for 2½ hours. The solution, filtered from the picric acid which crystallised on cooling, and freed from the remaining picric acid by extraction with ether, left the bromide on evaporation as a yellow residue (3·5 g.). Recrystallised from glacial acetic acid (10 c.c.) and ether (1 c.c.), it formed hard, hemispherical clusters of small, monoclinic prisms, m. p. 289—290° (decomp.). It is very soluble in water and deliquescent (Found: C, 47·5; H, 7·3; Br, 28·9; equiv., by titration with sodium hydroxide and phenolphthalein, 277. $C_{11}H_{20}O_2NBr$ requires C, 47·5; H, 7·25; Br, 28·8%; equiv., 278).

The *picrate*, precipitated by the addition of an alcoholic solution of picric acid (0·45 g.) to an aqueous solution of the bromide (0·55 g.), formed golden-yellow, hexagonal prisms (from alcohol), m. p. 169—170° (Found: N, 13·2. $C_{17}H_{22}O_9N_4$ requires N, 13·1%).

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CCCXLV.—*The Configuration of the Ammonium Ion.*

By WILLIAM HOBSON MILLS and ERNEST HENRY WARREN.

OF the views which have been put forward respecting the spatial configuration of the ammonium salts, those deserving of more serious consideration assign to the four positive radicals attached to the nitrogen atom a disposition which is either tetrahedral or pyramidal, these being the only arrangements in which the valencies of the nitrogen atom linking these radicals can be represented as inter-equivalent.

FIG. 1.

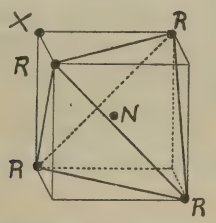
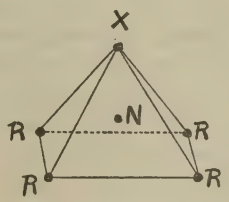


FIG. 2.



The suggestion of a tetrahedral distribution (Fig. 1) was first made, as is well known, by van 't Hoff ("Ansichten über die org. Chemie," 1878, p. 80), long before Pope and Peachey (J., 1899, **75**, 1127) opened the way to the experimental investigation of the stereochemistry of the ammonium salts.

The pyramidal formula (Fig. 2) was proposed by Bischoff (*Ber.*, 1890, **23**, 1197).

As long as nitrogen was regarded as being truly quinquevalent in the ammonium salts and the constitution of these compounds was considered to correspond with the symbol I the pyramidal formula appeared *a priori* at least as probable as the tetrahedral,

(I.) $\begin{matrix} R \\ R \\ R \\ R \end{matrix}\!\!\rangle N{-}X$ $\qquad$ $\left[\begin{matrix} R & & R \\ & N & \\ R & & R \end{matrix}\right]^{+}X$ (II.)

and a careful review of the then available evidence led Jones (J., 1905, **87**, 1782; *Rep. Brit. Assoc.*, 1904, 188; compare, however,

Jones and Dunlop, J., 1912, **101**, 1748) to the view that the pyramidal formula was the more in accordance with the experimental facts; this configuration of the ammonium salts is still represented as the most probable in some of the newer text-books of organic chemistry.

At the present time, however, largely through the development of electronic theories of valency and the clearer insight which these have afforded into the relation between ionising and non-ionising linkings, there exists a general tendency to assign to the ammonium salts a constitution (II) akin to that proposed by Werner (*Z. angew. Chem.*, 1906, **19**, 1345). But if the ammonium salts are thus constituted, then, as Werner pointed out (" Stereochemie," p. 311), the four positive radicals are, in all probability, tetrahedrally disposed about the nitrogen atom.

Whilst, therefore, on general grounds the tetrahedral configuration of the ammonium salts must at the present time be regarded as the most probable, no direct experimental evidence has hitherto been obtained which enables a definite decision to be made between this and the pyramidal configuration. The formation of the tertiary amine oxides, for example, and their molecular dissymmetry (when the three hydrocarbon radicals are different), which was demonstrated by Meisenheimer (*Ber.*, 1908, **41**, 3966; *Annalen*, 1911, **385**, 117), can be represented by means of either formula.

We have accordingly attempted to find some crucial experimental test which would decide between these two configurations. We have therefore prepared and examined the salts of a spirocyclic ammonium radical of the type III.

$$\left[\begin{matrix}H\\R'\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\!\!>\!N\!<\!\!\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}\!\!>\!C\!<\!\!\begin{matrix}H\\R''\end{matrix}\right]X \quad \text{(III.)}$$

The readiness with which the formation of these spirocyclic compounds takes place shows that there can be little strain in the two rings. The relative positions of the four carbon atoms attached to the central nitrogen atom must therefore approximate closely to those of the corresponding atoms in the simpler quaternary ammonium salts like tetramethyl- or tetraethyl-ammonium chloride. On the pyramidal formula, therefore, the positive ion of such a salt would have the configuration shown in Fig. 3, whilst on the tetrahedral formula its configuration would be represented by Fig. 4, the rings being represented plane for simplicity.

In Fig. 3 the four radicals RR'R'' lie in one vertical plane with the nitrogen atom, and this plane is clearly a plane of symmetry of the molecule. If, therefore, the simple quaternary ammonium salts have the pyramidal configuration, a compound of the formula (III) cannot show optical activity in solution.

If, however, the ion has the configuration represented in Fig. 4, it possesses no element of symmetry. It is non-superposable on its mirror image and the salts should be capable of resolution into optically active enantiomerides. Resolution of a salt of the type III into optically active components would therefore constitute a definite experimental proof that in the ammonium salts the four positive radicals are not arranged pyramidally about the nitrogen atom.

The resolution of salts of a spirocyclic ammonium radical, trimethylenetetrahydro*iso*quinolinium, was attempted by Jones and Dunlop (*loc. cit.*) with negative results. These salts are molecularly dissymmetric on the pyramidal but not on the tetrahedral theory of the configuration of the ammonium salts.

FIG. 3.

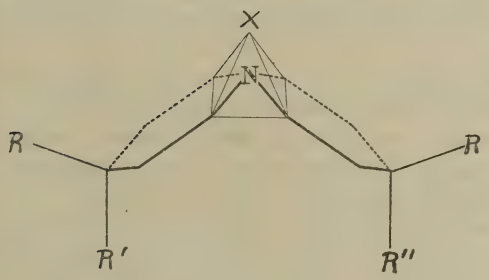
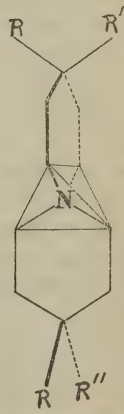


FIG. 4.



The compound which we chose for examination was 4-*phenyl*-4′-*carbethoxybispiperidinium*-1 : 1′-*spiran bromide* (III; R′ = Ph, R″ = CO_2Et, X = Br), which we prepared by the interaction of 4-phenylpiperidine (Bally, *Ber.*, 1887, **20**, 2590) with ethyl αε-dibromopentane-γ-carboxylate (see Mills and Bains, preceding paper).

On converting the pure *spiro*ammonium bromide into the *d*-α-bromocamphor-π-sulphonate, a mixture of diastereoisomeric salts was produced, by fractional crystallisation of which from acetone and ether and finally from acetone alone the optically pure d-spiro*ammonium* d-*bromocamphorsulphonate* was obtained. It gave in aqueous solution a molecular rotation for the mercury green light which exceeded by nearly 50° that due to the bromocamphorsulphonic ion. On removal of the latter by precipitating the sparingly soluble spiro*ammonium iodide* with aqueous sodium iodide a dextrorotatory iodide was obtained and this was converted with silver

bromide into the more soluble spiro*ammonium bromide*, the molecular rotation, $[M]_{5461}$, of which in aqueous solution was + 50·5°. The molecular rotation of the *spiro*ammonium bromide in aqueous solution is thus of the magnitude indicated approximately by the molecular rotation of the *d*-bromocamphorsulphonate.

The *d*-bromocamphorsulphonates left in the acetone–ether mother-liquors were converted into the l-*bromocamphorsulphonates* (with the aid of *l*-bromocamphorsulphonic acid prepared from *l*-camphor kindly given to us by Sir William Pope) and by fractional crystallisation of these the l-spiro*ammonium* l-*bromocamphorsulphonate* was obtained. This gave on conversion into the bromide the optically pure l-spiro*ammonium bromide* showing a molecular rotation, $[M]_{5461}$, of − 50·8°, which is thus, within the limits of experimental error, equal and opposite to that of the *d*-bromide.

These observations show definitely that this *spiro*ammonium ion possesses molecular dissymmetry. It therefore cannot have the configuration represented in Fig. 3. An experimental proof is thus given that the four positive radicals in the ammonium salts are not arranged about the nitrogen atom as assumed in the pyramidal theory.

The experimental evidence with regard to the configuration of the ammonium salts can now be stated briefly as follows :

(1) *Ammonium salts of the type* (N*abcd*)X *can be resolved into optically active antipodes.* The four radicals and the nitrogen atom in the ammonium ion therefore do not lie in one plane.

(2) *Ammonium salts of the type* (N*abcc*)X *are non-resolvable.* The ion $(Nabcc)^+$ therefore possesses a plane of symmetry, which must obviously be the plane which passes through *a*, *b*, and N and the line joining the two remaining radicals *c* must be perpendicular to this plane and bisected by it.

(3) *Isomerism, other than enantiomerism, dependent on the relative positions of substituent groups has never been observed in ammonium salts.* This indicates that the valencies by which the four radicals in the quaternary ammonium ion are attached to the nitrogen atom are inter-equivalent. The same conclusion is to be drawn from (2), since there can be no reason why the two radicals designated *a* and *b* should always be attached by a particular pair of valencies. Although this negative evidence has not the same weight as positive evidence would have, the experimental work on which it rests is very extensive, and the inter-equivalency of the four co-valencies of nitrogen in the ammonium salts can be regarded as practically established. But this inter-equivalence of the valencies requires that they must be separated by equal angular intervals.

The positions which can be occupied by the radicals *c* are thus limited to those shown in Fig. 5 and Fig. 6. In other words, the only configurations for the ammonium ion which accord with the foregoing observations are those in which the radicals have either a pyramidal * or a tetrahedral distribution about the nitrogen atom.

(4) *Spirocyclic ammonium salts of the type III are molecularly asymmetric.* This excludes the pyramidal configuration. The conclusion must therefore be drawn that *in the quaternary ammonium ion the four radicals are disposed tetrahedrally about the nitrogen atom,* and that the configuration of the spirocyclic ammonium ion is that represented in Fig. 4.

It must also be concluded that in the simple ammonium salts the four hydrogen atoms of the ammonium radical are similarly tetrahedrally distributed about the nitrogen atom.

Fig. 5.

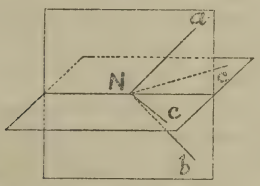
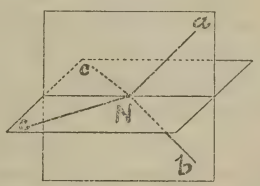


Fig. 6.



The view that the ammonium ion, NH_4^+, and the methane molecule, CH_4, have corresponding configurations, the probability of which is evident on the electronic theory of molecular structure (since each complex is composed of a positive nucleus, four hydrogen nuclei, and ten electrons), is thus confirmed by experimental stereochemical evidence.

Experimental.

dl-4-*Phenyl*-4′-*carbethoxybispiperidinium*-1 : 1′-*spiran Bromide.*—This compound was prepared by the condensation of ethyl di-β-bromoethylacetate (Mills and Bains, *loc. cit.*) with 4-phenylpiperidine (2 mols.) (Bally, *loc. cit.*) in boiling benzene solution. The preparation is greatly facilitated by the fact that the spiran bromide crystallises almost at once from the boiling solution, whilst the phenylpiperidine hydrobromide (although practically insoluble in boiling benzene) remains in supersaturated solution.

* The pyramidal formula would, however, as has long been recognised, render probable the existence of a never observed isomerism corresponding with that of the platosammine and platosemidiammine chlorides and that of the isomeric dimethyltellurium iodides of Vernon (J., 1920, **117**, 86, 889).

The ester (4·8 g.) and the base (6 g.) were dissolved in benzene (200 c.c.) and the mixture was filtered hot after gently boiling for 6 hours. The crystalline product, recrystallised from alcohol and ether, gave small platelets, m. p. 276—277° (decomp.). Slow crystallisation from ethyl acetate containing a trace of alcohol gave fine needles of the same m. p. The salt is extremely soluble in water or alcohol, but is insoluble in ether or benzene, and also in ethyl acetate, chloroform, or acetone if these are free from alcohol (Found : C, 59·6; H, 7·4; N, 3·9; Br, 20·8. $C_{19}H_{28}O_2NBr$ requires C, 59·7; H, 7·3; N, 3·7; Br, 20·9%).

dl-4-*Phenyl*-4′-*carbethoxybispiperidinium*-1 : 1′-*spiran Iodide*.—This salt is precipitated by the addition of saturated sodium iodide solution to a concentrated aqueous solution of the *spiro*ammonium bromide. It is formed as an oil, which solidifies when scratched, and gives prismatic crystals, m. p. 209—210°, when crystallised from alcohol and ether. It is insoluble in ethyl acetate or chloroform, and is practically insoluble in water. It dissolves in alcohol to the extent of 1·5% (Found : C, 52·8; H, 6·5; N, 3·0; I, 29·5. $C_{19}H_{28}O_2NI$ requires C, 53·1; H, 6·5; N, 3·25; I, 29·6%).

d-4-*Phenyl*-4′-*carbethoxybispiperidinium*-1 : 1′-*spiran* d-α-*Bromo*-π-*camphorsulphonate*.—An aqueous solution of the *spiro*ammonium bromide was treated with the equivalent quantity of silver bromocamphorsulphonate. Evaporation under diminished pressure of the filtrate from the silver bromide gave a gummy residue, which was repeatedly crystallised from acetone and ether, and finally from acetone alone. The successive crops showed a progressive readiness to crystallise, a rising melting point, and an increasing specific rotation. The polarimetric values found for the crops obtained from the last three crystallisations in aqueous solution, using the mercury yellow and green light, were (c = 0·984—0·986) $[\alpha]^{18°}_{5780}$ + 55·9°, 55·7°, and 55·6°; $[\alpha]^{18°}_{5461}$ + 64·5°, 64·7°, 64·5°. They were therefore regarded as being optically pure. The compound forms delicate, silky needles attaining a length of 2 cm. or so, m. p. 210—212° with softening at 195° (Found : Br, 13·1. $C_{29}H_{43}O_6NBrS$ requires Br, 13·0%).

Further polarimetric values found for the last crop in aqueous solution were (c = 1·864, 1·855) $[\alpha]^{18°}_{5780}$ + 55·2°, 55·3°; $[\alpha]^{18°}_{5461}$ + 64·6°, 64·75°.

The means of all these values give for the molecular rotations of the salt in aqueous solution (c = 1—2) $[M]^{18°}_{5780}$ + 339°, $[M]^{18°}_{5461}$ + 395·5°. Subtracting the corresponding values for the bromocamphorsulphonic ion, $[M]^{18°}_{5780}$ + 295°, $[M]^{18°}_{5461}$ + 346·5°, we obtain $[M]^{18°}_{5780}$ + 44°, $[M]^{18°}_{5461}$ + 49° as the molecular rotations of the *spiro*ammonium ion. These values agree, within the limits of experi-

mental error (seeing that they result from the difference of three figure numbers), with those found by direct observation on the bromide (see below), $[M]^{20°}_{5780}$ + 44·9°, $[M]^{20°}_{5461}$ + 50·5°.

d-4-*Phenyl*-4′-*carbethoxybispiperidinium*-1 : 1′-*spiran Iodide*.—A saturated solution of sodium iodide was added gradually to an aqueous solution of the *d-spiro*ammonium *d*-bromocamphorsulphonate, stirred so that the precipitate was obtained crystalline. Crystallised from alcohol and ether, it formed granular crystals, m. p. 222—223°. It thus melts 13° higher than the racemic salt (Found : C, 53·25; H, 6·4; I, 29·6. $C_{19}H_{28}O_2NI$ requires C, 53·1; H, 6·5; I, 29·6%).

The following polarimetric observations were made on the alcoholic solution :

$l = 4$; $c = 1·562$; $\alpha^{20°}_{5780}$ + 0·556°; $\alpha^{20°}_{5461}$ + 0·608°;
whence $[\alpha]^{20°}_{5780}$ + 8·9°; $[\alpha]^{20°}_{5461}$ + 9·7°.

d-4-*Phenyl*-4′-*carbethoxybispiperidinium*-1 : 1′-*spiran Bromide*.—The *d*-iodide was treated in hot water with silver bromide, and the filtrate evaporated under diminished pressure. The dried residue, crystallised from a mixture of ethyl alcohol, ethyl acetate, and a little ether, gave the pure bromide as needles, m. p. 274—275° (decomp.) (Found : Br, 20·6. Calc., Br, 20·9%). The compound gave the following values in aqueous solution :

$l = 4$; $c = 2·122$; $\alpha^{20°}_{5780}$ + 1·00°; $\alpha^{20°}_{5461}$ + 1·125°;
whence $[\alpha]^{20°}_{5780}$ + 11·76°; $[\alpha]^{20°}_{5461}$ + 13·23°; $[M]^{20°}_{5780}$ + 44·9°; $[M]^{20°}_{5461}$ + 50·5°.

l-4-*Phenyl*-4′-*carbethoxybispiperidinium*-1 : 1′-*spiran* l-*Bromocamphorsulphonate*.—The mother-liquors containing the *spiro*ammonium *d*-bromocamphorsulphonate were evaporated to dryness and the gummy residue was converted into the iodide by means of aqueous sodium iodide solution. The iodide thus obtained was deeply coloured with periodide, but was obtained colourless after three or four recrystallisations.

The iodide was treated with its equivalent of silver *l*-bromocamphorsulphonate in hot aqueous alcoholic solution, and the filtrate evaporated to dryness under diminished pressure. The gummy mass was dissolved in warm acetone and, after the addition of a little ether, was allowed to stand for a day or so to crystallise. Crystallisation took place more readily and with better yield than in the original preparation of the *d-spiro*ammonium *d*-bromocamphorsulphonate, owing presumably to the previous removal of some of the *d*-enantiomorph.

After four or five recrystallisations the salt gave the following specific rotations in aqueous solution :

$[\alpha]^{17°}_{5780}$ — 54·2°, $[\alpha]^{17°}_{5461}$ — 64·1°.

After a further recrystallisation the values obtained were :

$$[\alpha]^{17^\circ}_{5780} - 54{\cdot}25^\circ,\ [\alpha]^{17^\circ}_{5461} - 64{\cdot}1^\circ.$$

The melting point was 210—212° with softening at 195°.

As the rotation was not altered by further crystallisation, this last crop was employed for preparation of the *l*-iodide.

1-4-*Phenyl*-4′-*carbethoxybispiperidinium*-1 : 1′-*spiran Iodide*.—The *l*-*spiro*ammonium *l*-bromocamphorsulphonate was converted into the iodide by the same method as was used in the *d*-series. The melting point was the same as that of the *d*-iodide, 222—223°. A mixture of the *d*- and *l*-iodides in equal proportions melted at practically the same temperature as the *dl*-iodide, 209—211° (Found : I, 29·6. Calc., I, 29·6%). The specific rotations in ethyl-alcoholic solution were in good agreement with those found for the *d*-salt :

$l = 4$; $c = 0{\cdot}589$; $\alpha^{20^\circ}_{5780} - 0{\cdot}200^\circ$; $\alpha^{20^\circ}_{5461} - 0{\cdot}233^\circ$;

whence $[\alpha]^{20^\circ}_{5780} - 8{\cdot}5^\circ$; $[\alpha]^{20^\circ}_{5461} - 9{\cdot}9^\circ$.

1-4-*Phenyl*-4′-*carbethoxybispiperidinium*-1 : 1′-*spiran Bromide*.—The *l*-iodide was converted into the *l*-bromide by the same method as was used in the *d*-series. The following polarimetric observations were made on the salt in aqueous solution :

$l = 4$; $c = 2{\cdot}02$; $\alpha^{20^\circ}_{5780} - 0{\cdot}95^\circ$; $\alpha^{20^\circ}_{5461} - 1{\cdot}075^\circ$; $\alpha^{20^\circ}_{4359} - 1{\cdot}81^\circ$;

whence $[\alpha]^{20^\circ}_{5780} - 11{\cdot}75^\circ$; $[\alpha]^{20^\circ}_{5461} - 13{\cdot}3^\circ$; $[\alpha]^{20^\circ}_{4359} - 22{\cdot}4^\circ$;

and $[M]^{20^\circ}_{5780} - 44{\cdot}9^\circ$; $[M]^{20^\circ}_{5461} - 50{\cdot}8^\circ$; $[M]^{20^\circ}_{4359} - 85{\cdot}5^\circ$.

The molecular rotations found for the enantiomorphous bromides in aqueous solution are thus for the mercury yellow light + 44·9° and − 44·9°, and for the mercury green + 50·5° and − 50·8°. This concordance confirms the view that the resolution was complete.

We desire to express our thanks to the Department of Scientific and Industrial Research for a maintenance grant to one of us (E. H. W.) which enabled him to take part in this work.

University Chemical Laboratory,
Cambridge. [*Received, September 10th*, 1925.]

CCCXLVI.—*The Correlation of Absorption Spectra with Ionisation in Violuric Acid.*

By Richard Alan Morton and Arthur Harold Tipping.

Violuric acid is faintly yellow in the crystalline state and pink in aqueous solution. The correspondence between concentration of violurate ion and depth of colour roughly established by colorimetric observations has now been accurately confirmed by the quantitative

methods of sector-photometry and absorption spectroscopy. Solutions of the acid in the purest conductivity water containing small quantities of hydrochloric acid were examined spectrographically, and their p_H values determined by means of the quinhydrone electrode.

TABLE I.

Solution.	Mol. conc. of violuric acid.	Mol. conc. of HCl.	p_H at 18°.
a	0·01	nil	3·36
b	0·0099	0·0001	3·32
c	0·0095	0·0005	3·194
d	0·0090	0·0010	3·03

From the p_H value for 0·01M-violuric acid the dissociation constant at 18° is found :

$$K_{18°} = [H^+][Vi^-]/[HVi] = (10^{-3·36})^2/(10^{-2} - 10^{-3·36}) = 1·992 \times 10^{-5}.$$

From this constant the concentrations of violurate ion in the solutions b, c, and d may be calculated.

TABLE II.

Solution.	Conc. of Vi ion.	d.	Log (I_0/I).	e max. (for ion).
a	0·0004365	30 cm.	0·8	61·09
b	0·000395	,,	0·7	59·07
c	0·000285	,,	0·55	64·33
d	0·000188	,,	0·325	57·37
			Mean	60·46

In the equation $\log (I_0/I) = e\,c\,d$, I_0/I is the ratio of the intensities of the incident and the emergent light, c is the concentration of the absorbing solute in gram-ions per litre, and d is the thickness of the absorbing layer; e is then the molecular extinction coefficient. In photographing the absorption spectrum, the value of $\log I_0/I$ was increased for successive exposures. The values recorded in Table II are the highest for which definite match points could be seen; the accuracy was about 1 in 15. Within the limits of error, therefore, the colour intensity is proportional to the concentration of violurate ion.

Addition of alkali caused an increase in the absorptive power of the solute.

TABLE III.

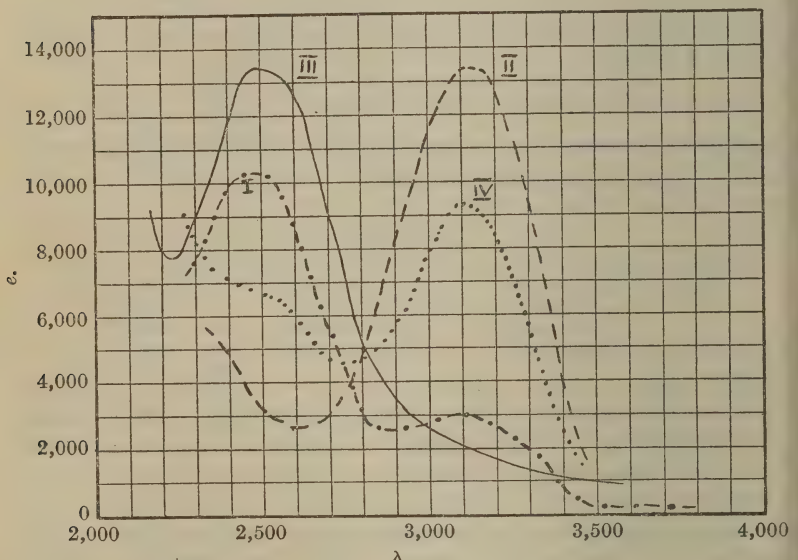
Mol. conc. of violuric acid.	Conc. of alkali.	Log (I_0/I).	d, cm.
0·0066	0·0033	1·6	8
0·0025	0·0025	1·17	8
0·01	0·0008	1·1	30
		or 0·29	8

The alkali violurate is almost completely dissociated in solution. If the observed increase in intensity of colour is due to increased

concentration of violurate ion, p_H-measurements should indicate a molecular extinction coefficient of about 60. In the case of 0·0025*M*-sodium violurate, $p_H = 8·41$, the ionic concentration is 0·0025, and e (max.) is 58·5. Similarly, for the 0·0066*M*-violuric acid solution, which is 0·0033*M* with respect to alkali, $p_H = 4·82$ and e (max.) is 53.

These results do not differ very much. It seemed likely that the addition of sodium chloride, which would repress the ionisation, would lead to interesting results. Photographs of the absorption

FIG. 1.



—·— I. *Violuric acid in water.*
— — — II. 0·0009*M-aqueous violuric acid and* 0·002*M-potassium hydroxide.*
——— III. *Violuric acid in alcohol.*
. . . . . IV. *Violuric acid M*/1000, *potassium hydroxide M*/2000.

spectra of solutions of sodium violurate containing excess of sodium chloride were therefore taken, compensating cells containing the same concentration of sodium chloride being used to counterbalance any loss of transmissive power due to this salt.

TABLE IV.

Mol. conc. of sodium violurate	0·0033	0·0025	0·0017
Mol. conc. of sodium chloride	6·24	4·16	2·08
e (max.)	56·25	55·0	54·75

The absorptive power of undissociated sodium violurate is therefore of the order $e = 55$. The head of the absorption band is near 538 μμ.

The spectrum of violuric acid has been examined in the ultra-violet region also. For the aqueous solution, two bands were found, one at λ (max.) = 3120 Å. and *e* (max.) 3000 and the other at 2490 Å. and *e* (max.) 10,300. A solution 0·0009*M* with respect to violuric acid and 0·002*M* with respect to potassium hydroxide would certainly consist of hydroxide and completely dissociated potassium violurate. This solution shows one absorption band, λ (max.) = 3130 Å., *e* (max.) 13,300.

It is striking that, for an aqueous solution in which the acid is incompletely dissociated, two bands are obtained whose extinctions are together equal to 13,300. The band at 3130 Å. is common both to the acid and to the alkaline solution and may therefore be ascribed to the ion. If, then, the other band is due to the undissociated acid, an alcoholic solution of violuric acid should show only this band. Actually, one band is observed, λ (max.) = 2516 Å., *e* (max.) = 13,400, and the extinction is the same as that of the dilute alkaline solution. There can be no doubt, therefore, that the bands at 250 and 312 μμ are due respectively to the undissociated acid and the ion. The graph shows that an intermediate stage was found, as was to be expected.

We wish to express our gratitude to Dr. J. W. Corran for assistance with the quinhydrone electrode and to Professor E. C. C. Baly, C.B.E., F.R.S., for suggesting the investigation. One of us (A. H. T.) is indebted to the Advisory Council of the Department of Scientific and Industrial Research for a maintenance grant.

THE UNIVERSITY, LIVERPOOL. [*Received, July 9th,* 1925.]

CCCXLVII.—*The Parachor and Chemical Constitution. Part III. Orientation Isomerism in Aromatic Compounds.*

By SAMUEL SUGDEN and HENRY WILKINS.

IT has been shown in previous papers that in two classes of isomeric substances, namely, metameric esters (Sugden, J., 1924, **125**, 1185) and geometrical isomerides (Sugden and Whittaker, this vol., p. 1868), differences in constitution produce little or no change in the value of the parachor. The isomerism of these substances involves only a rearrangement of groups and linkings which does not alter the degree of unsaturation of the compound.

In the present paper, data are presented for a number of disubstituted benzene derivatives. These are of interest, since in many

cases, *e.g.*, the chloro- and bromo-nitrobenzenes, the isomerides differ markedly in the reactivity of the halogen atom. Further, it has been shown previously (Sugden, *loc. cit.*) that the data of Turner and Merry (J., 1910, **97**, 2075) give, for *m*-toluonitrile, a much lower parachor than is found for the *o*- and *p*-isomerides. We have therefore determined the surface tension and density of a number of orientation isomerides of this type, and the parachors calculated from the data thus obtained are collected in Table I.

The constants for the xylenes are derived from the measurements of Schiff (*Annalen*, 1884, **223**, 47), those for *p*-nitrotoluene and *p*-chloronitrobenzene from the observations of Sugden (J., 1924, **125**, 1167), and the remainder from new measurements, details of which are given in the experimental portion of this paper.

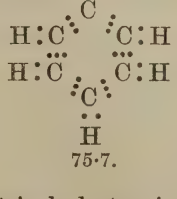
TABLE I.

	Ortho.	Meta.	Para.	Calc.
Xylenes	283·3	283·8	283·8	285·1
Nitrotoluenes	301·1	300·6	302·8	303·1
Chloronitrobenzenes	299·9	298·9	300·0	301·2
Bromonitrobenzenes	312·9	313·5	313·5	315·0
Toluonitriles	290·6	295·6	294·4	292·9

It will be seen from the table that, within the limits of experimental error (about ± 2 units), there is no appreciable difference between the parachors of ortho-, meta-, and para-isomerides, but that all the substances studied give constants in good agreement with the theoretical values tabulated in the last column. We have failed to confirm the lower value for *m*-toluonitrile obtained from Turner and Merry's data, and find that this substance behaves normally.

It has been assumed in previous papers on the parachor that benzene and its derivatives have the Kekulé formula (I), for which the structural constant to be added to the sum of the atomic constants to obtain the calculated value of the parachor would be

(I.)  75·7.



(II.) 75·7.

(III.)  70·4.

75·7 units. The symmetrical electronic structure (II) should give the same constant, since it represents an equal degree of unsaturation, but the Dewar formula (III) should give a smaller constant

70·4.* The good agreement between the observed and the calculated parachors shows that the Kekulé formula or formula II will serve to reproduce the experimental figures. It is interesting to note, however, that in all cases but two the observed parachor is lower than the theoretical figure. This is not inconsistent with the theory of Ingold (J., 1922, **121**, 1123) that benzene and its derivatives are equilibrium mixtures of tautomerides, one of which possesses the bridged structure (III).

It is evident from the data for the chloro- and bromo-nitrobenzenes that the reactivity of the halogen atom in the ortho- and para-compounds and its inertness in the meta-compound are not due to differences in the molecular volume, for the three isomerides have almost exactly the same parachor. This result was not unexpected, since it has been found in other cases (this vol., p. 1868) that isomerides possessing the same degree of unsaturation show no differences in their parachor. The structural constants which have to be added to the sum of the atomic constants in calculating the parachor appear to depend chiefly on the degree of unsaturation, *i.e.*, on the crowding of electronic orbits, and if the reactivity of the halogen atoms is explained by the concentration of electrons about alternate carbon atoms the effect of the sparseness of distribution about the other three carbon atoms would act in the opposite direction, so that the total effect on the parachor would be very small.

The good agreement between the observed and the calculated values for the three toluonitriles gives further evidence for the view expressed in a previous paper (Sugden, *loc. cit.*, p. 1186 †) that the triple bond in the CN group has the same effect on the parachor as that in acetylene derivatives. There is no need, therefore, to assume that this radical has the special structure, suggested by Langmuir (*J. Amer. Chem. Soc.*, 1919, **41**, 905), of two nuclei within a single octet.

Experimental.

In the course of this work new measurements have been made of the surface tension and density of ten disubstituted benzene derivatives over a range of temperatures. Surface tensions were determined by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 858; 1924, **125**, 27). The constants for the bubblers used are: Apparatus 4d, 5a, 5b; r_2 0·139, 0·140, 0·140 cm.,

* This figure is obtained by adding the constants for two double bonds and two four-membered rings.

† On this page, in the second line below the table, for "hydrogen" read "nitrogen."

respectively ; *A* 0·007767, 0·006805, 0·009655, respectively. Densities were determined by the U-shaped pyknometer described previously (J., 1924, **125**, 1171) and are given in g./c.c. All temperatures quoted are corrected by comparison with a standard thermometer with an N.P.L. certificate and are corrected for exposed stem.

The tables below are set out in the same manner as those in previous papers of this series and do not need further description. The parachor in the last column is calculated by the formula

$$[P] = \gamma^{1/4}M/(D - d),$$

where γ is the surface tension, M the molecular weight, D the density of the liquid, and d the density of the vapour. For the substances studied in the present paper, d is very small and has been neglected.

o-*Nitrotoluene* was fractionated; the portion used boiled at 219—219·5° (corr.)/762 mm. Densities determined : $D_4^{18\cdot5°}$ 1·162, $D_4^{36°}$ 1·146, $D_4^{56\cdot5°}$ 1·126, $D_4^{79°}$ 1·103, whence $D_4^{t°} = 1\cdot180 - 0\cdot00098\,t$.

App.	*t*.	*P*.	*D*.	ϕ.	γ.	Parachor.
4d	19·5°	5266	1·161	1·0207	41·76	300·1
,,	44·5	4873	1·136	1·0220	38·69	300·9
,,	62·5	4627	1·119	1·0228	36·76	301·6
,,	79·0	4363	1·102	1·0238	34·70	301·9
					Mean	301·1

m-*Nitrotoluene* was purified by repeated freezing; the specimen used melted at 16° (corr.). Densities determined : $D_4^{20°}$ 1·161, $D_4^{37°}$ 1·145, $D_4^{59°}$ 1·124, $D_4^{89°}$ 1·101, $D_4^{121°}$ 1·063, whence $D_4^{t°} = 1\cdot180 - 0\cdot00095\,t$.

App.	*t*.	*P*.	*D*.	ϕ.	γ.	Parachor.
5a	20°	5971	1·161	1·018	41·36	299·4
,,	42	5586	1·140	1·019	38·73	300·0
,,	64	5240	1·119	1·020	36·37	300·9
,,	91	4811	1·094	1·0215	33·45	301·3
,,	116	4385	1·070	1·023	30·53	301·2
					Mean	300·6

o-*Chloronitrobenzene* was recrystallised from ligroin. The specimen used melted sharply at 33° (corr.). Densities determined : $D_4^{45\cdot5°}$ 1·348, $D_4^{71\cdot5°}$ 1·320, $D_4^{92\cdot5°}$ 1·297, $D_4^{111\cdot0°}$ 1·276, whence $D_4^{t°} = 1\cdot398 - 0\cdot00110\,t$.

App.	*t*.	*P*.	*D*.	ϕ.	γ.	Parachor.
4d	50·5°	5318	1·342	1·0238	42·29	299·2
,,	70·5	4999	1·320	1·0249	39·80	299·7
,,	91·5	4669	1·297	1·0262	37·23	299·9
,,	121	4263	1·265	1·0279	34·04	300·8
					Mean	299·9

m-*Chloronitrobenzene* was recrystallised from absolute alcohol and melted sharply at 46° (corr.). Densities determined: $D_4^{50°}$ 1·343, $D_4^{58°}$ 1·336, $D_4^{76°}$ 1·314, $D_4^{85°}$ 1·304, $D_4^{93°}$ 1·296, $D_4^{127°}$ 1·257, whence $D_4^{t°} = 1·398 - 0·00111\,t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
4d	60·5°	5255	1·331	1·0238	41·79	300·9
„	74·5	4867	1·315	1·0255	38·76	298·9
„	90·5	4546	1·298	1·0269	36·27	297·8
„	129	3974	1·255	1·0297	31·77	298·0
					Mean	298·9

o-*Bromonitrobenzene* was recrystallised from absolute alcohol; the specimen used melted at 39° (corr.). Densities determined: $D_4^{53·5°}$ 1·664, $D_4^{64°}$ 1·650, $D_4^{75°}$ 1·635, $D_4^{85°}$ 1·622, whence $D_4^{t°} = 1·735 - 0·00133\,t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
5b	55·5°	5436	1·661	1·0287	43·44	312·2
„	67·5	5267	1·645	1·0294	42·12	312·8
„	80	5068	1·629	1·0302	40·56	313·0
„	94·5	4863	1·609	1·0311	38·94	313·7
					Mean	312·9

m-Bromonitrobenzene was recrystallised from absolute alcohol and melted sharply at 55·5° (corr.). Densities determined: $D_4^{59·5°}$ 1·651, $D_4^{70·5°}$ 1·636, $D_4^{82°}$ 1·621, $D_4^{90°}$ 1·612, whence $D_4^{t°} = 1·728 - 0·00130\,t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
4d	63°	5310	1·646	1·0292	42·45	313·3
„	71·5	5172	1·635	1·0297	41·36	313·3
„	83	5010	1·620	1·0304	40·10	313·9
„	91	4863	1·610	1·0311	38·94	313·5
					Mean	313·5

p-*Bromonitrobenzene* was recrystallised from absolute alcohol and melted sharply at 127° (corr.). Densities determined: $D_4^{139°}$ 1·563, $D_4^{142·5°}$ 1·552, $D_4^{154°}$ 1·536, $D_4^{164°}$ 1·523, whence $D_4^{t°} = 1·736 - 0·00130\,t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
4d	132°	4304	1·564	1·0342	34·58	313·3
„	145	4119	1·547	1·0353	33·12	313·3
„	159·5	3947	1·529	1·0364	31·78	313·7
„	170	3800	1·515	1·0375	30·63	313·7
					Mean	313·5

o-*Toluonitrile* was redistilled four times; the fraction used boiled at 205—205·5° (corr.)/759 mm. Densities determined: $D_4^{26°}$ 0·993, $D_4^{56°}$ 0·976, $D_4^{75°}$ 0·965, $D_4^{95°}$ 0·948, whence $D_4^{t°} = 1·017 - 0·00072\,t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
4d	51°	4457	0·980	1·0207	35·34	291·4
„	69	4200	0·967	1·0217	33·33	291·0
„	90	3897	0·952	1·0230	30·96	290·2
„	116·5	3570	0·933	1·0246	28·41	289·8
					Mean	290·6

m-*Toluonitrile* was redistilled; the fraction used boiled at 213° (corr.)/759 mm. Densities determined: $D_{4^\circ}^{18\cdot5^\circ}$ 0·987, $D_{4^\circ}^{40\cdot5^\circ}$ 0·969, $D_{4^\circ}^{61\cdot5^\circ}$ 0·953, $D_{4^\circ}^{79\cdot5^\circ}$ 0·936, whence $D_{4^\circ}^{t^\circ} = 1\cdot003 - 0\cdot00082\,t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
4d	18·5°	4827	0·988	1·0193	38·20	294·7
,,	47	4435	0·964	1·0205	35·16	295·8
,,	64·5	4177	0·950	1·0214	31·14	295·8
,,	86·5	3889	0·932	1·0225	30·88	296·2
					Mean	295·6

The purity of this specimen was further tested by hydrolysing it to the corresponding acid with caustic potash. The crude product, obtained in 95% yield, melted at 105° and, after one recrystallisation, sharply at 112° (corr.) and was therefore pure *m*-toluic acid. Turner and Merry (*loc. cit.*) give densities for this substance which lead to the formula $D_{4^\circ}^{t^\circ} = 1\cdot048 - 0\cdot00080\,t$. These densities are much higher than those found by the authors and also much higher than the values found by Turner and Merry for the ortho- and para-isomerides. It seems probable that the specimen used by these workers was not sufficiently pure.

p-*Toluonitrile* was recrystallised from absolute alcohol and melted sharply at 29° (corr.). Densities determined: $D_{4^\circ}^{43^\circ}$ 0·971, $D_{4^\circ}^{61^\circ}$ 0·955, $D_{4^\circ}^{75^\circ}$ 0·945, $D_{4^\circ}^{93\cdot5^\circ}$ 0·931, whence $D_{4^\circ}^{t^\circ} = 1\cdot004 - 0\cdot00078\,t$.

App.	t.	P.	D.	ϕ.	γ.	Parachor.
4d	51·5°	4328	0·964	1·0210	34·32	294·1
,,	67·5	4116	0·951	1·0217	32·67	294·4
,,	82·5	3909	0·939	1·0226	31·05	294·3
,,	96	3754	0·929	1·0233	29·84	294·7
					Mean	294·4

One of us (S. S.) is indebted to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expense of this investigation.

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Fetter Lane, E.C. 4. [*Received, September 17th,* 1925.]

CCCXLVIII.—*The Conversion of* r-*Phenyl-α-naphthylglycollic Acid into Ketones.*

By Alex. McKenzie and Harold James Tattersall.

Since phenyl-α-naphthylglycollic acid was required for several purposes, a convenient method for its preparation is described in the present paper.

The dehydration of α-naphthylhydrobenzoin with cold concentrated sulphuric acid led to the formation of the compound obtained by the deamination of β-hydroxy-αβ-diphenyl-β-naphthylethylamine

(McKenzie and Roger, J., 1924, **125**, 844). This compound was subsequently shown to be diphenylacetonaphthone, but it was not the sole product of the dehydration in question, since the isomeric α-naphthyldeoxybenzoin also was isolated from the oil from which the naphthone had been partly separated. Some difficulty was experienced in separating the two isomerides in a state of purity, because they melt at practically the same temperature. The action of hot dilute sulphuric acid, when applied for the dehydration of α-naphthylhydrobenzoin, pursued a somewhat different course from that of the concentrated acid, inasmuch as three distinct isomerides, namely, naphthyldeoxybenzoin, diphenylnaphthylacetaldehyde and diphenylnaphthylethylene oxide, were shown to be present (McKenzie and Dennler, J., 1924, **125**, 2105). Meanwhile, the dehydration of α-naphthylhydrobenzoin was also under investigation by Tiffeneau and Orékhov (*Compt. rend.*, 1924, **178**, 1619), who isolated α-naphthyldeoxybenzoin by the use of concentrated sulphuric acid. Professor Tiffeneau kindly provided us with a specimen of his compound, and we were able to prove, by means of determinations of the melting point of the mixture and by the colour reaction with concentrated sulphuric acid, that it was identical with the α-naphthyldeoxybenzoin prepared in this laboratory. We have now prepared this ketone by a method which does not depend on a semipinacolinic transformation, and it is anticipated that the data which have been accumulated may in due course be of service in the field of optical activity.

A novel application of Grignard reagents was described by McKenzie and Boyle (J., 1921, **119**, 1131), who showed that the interaction of diphenylchloroacetyl chloride and magnesium phenyl bromide pursued an abnormal course. Neither β-benzopinacolin nor pentaphenylethanol was obtained, the product being phenyldeoxybenzoin (compare McKenzie and Roger, *loc. cit.*, p. 849). Phenyl-α-naphthylglycollic acid was accordingly converted by means of phosphorus pentachloride into phenyl-α-naphthylchloroacetyl chloride, which was then acted on by an excess of magnesium phenyl bromide. α-Naphthyldeoxybenzoin was thus obtained, and its formation may be attributed to the following changes :

$$\begin{matrix}C_6H_5\\C_{10}H_7\end{matrix}\!>\!C\!<\!\begin{matrix}Cl\\COCl\end{matrix} + 2MgPhBr = \begin{matrix}C_6H_5\\C_{10}H_7\end{matrix}\!>\!C{:}CO + Ph.Ph + 2MgClBr,$$

$$\begin{matrix}C_6H_5\\C_{10}H_7\end{matrix}\!>\!C{:}CO + MgPhBr = \begin{matrix}C_6H_5\\C_{10}H_7\end{matrix}\!>\!C{:}C\!<\!\begin{matrix}OMgBr\\Ph\end{matrix},$$

$$\begin{matrix}C_6H_5\\C_{10}H_7\end{matrix}\!>\!C{:}C\!<\!\begin{matrix}OMgBr\\Ph\end{matrix} + H_2O = \begin{matrix}C_6H_5\\C_{10}H_7\end{matrix}\!>\!C{:}C\!<\!\begin{matrix}OH\\Ph\end{matrix} + Mg\!<\!\begin{matrix}Br\\OH\end{matrix},$$

$$\begin{matrix}C_6H_5\\C_{10}H_7\end{matrix}\!>\!C{:}C\!<\!\begin{matrix}OH\\Ph\end{matrix} \longrightarrow \begin{matrix}C_6H_5\\C_{10}H_7\end{matrix}\!>\!CH{\cdot}COPh.$$

It is here assumed that the initial phase consists in the production of phenyl-α-naphthylketen. Now, Wilsmore and Deakin (J., 1905, **97**, 1968) have shown that acetone can be obtained from keten and magnesium methyl iodide, and the isolation of phenyldeoxybenzoin (designated at the time as triphenylvinyl alcohol) from diphenylketen and magnesium phenyl bromide (Staudinger, *Annalen*, 1907, **356**, 70) renders it probable that this application of Grignard reagents on ketens is applicable generally.

In the above scheme the final phase involves the desmotropy of a substituted vinyl alcohol. Although the introduction of aromatic groups into vinyl alcohol tends to make the configuration of the substituted compound much more stable than that of vinyl alcohol itself, as is shown by the isolation of phenyldiphenylenevinyl alcohol by Kurt Meyer and Gottlieb-Billroth (*Ber.*, 1921, **54**, 575), we have not observed that naphthyldeoxybenzoin exhibits any tendency to enolisation. It is not soluble in aqueous alkali, it gives no coloration with ferric chloride, nor does it decolorise an alcoholic solution of bromine. Moreover, it behaves as a typical ketone when acted on by magnesium methyl iodide, and its disruption with alcoholic potash is also in accordance with the ketonic structure.

Ketones were also isolated when phenyl-α-naphthylchloroacetyl chloride was acted on in a similar manner by the Grignard reagents prepared from methyl iodide, α-bromonaphthalene, and *p*-bromotoluene, respectively. Those substances displayed no enolic reactions; they did not decolorise an alcoholic solution of bromine, and they were sparingly soluble both in cold and in hot *N*-caustic soda. In accordance with the assumption that ketens are produced initially, it was noted that the solutions became coloured during the action of the acid chloride with the Grignard reagents, and the crude products after the decomposition of the magnesium complexes were resinous in appearance, possibly due to the presence of polymerised ketens.

Phenyl-α-naphthylglycollic acid was reduced by hydriodic acid and phosphorus to phenyl-α-naphthylacetic acid, and it was expected that α-naphthyldeoxybenzoin would result from the application of the Friedel and Crafts reaction on phenyl-α-naphthylacetyl chloride, thus; $C_{10}H_7 \cdot CHPh \cdot COCl \longrightarrow C_{10}H_7 \cdot CHPh \cdot COPh$. We were unable to obtain any evidence that the action took this course, and this was all the more surprising, since diphenylacetyl chloride behaves in the usual manner, giving phenyldeoxybenzoin with benzene and aluminium chloride (Klingemann, *Annalen*, 1893, **275**, 83), and diphenylacetonaphthone with naphthalene and aluminium chloride (McKenzie and Dennler, *loc. cit.*). One of the products was a compound melting at 115·5—116·5°, and its analysis

showed that the reaction had proceeded in a manner altogether unexpected, inasmuch as one molecular proportion of hydrogen chloride was eliminated from the acid chloride. Now, according to Böeseken (*Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 417; *Rec. trav. chim.*, 1913, **32**, 1; compare also Wieland and Bettag, *Ber.*, 1922, **55**, 2246), the initial attack of the aluminium chloride during a Friedel and Crafts reaction is not on the hydrocarbon but on the acid chloride. In the case we have studied, it is not unlikely that an additive compound of the acetyl chloride and aluminium chloride was formed, in which compound both the hydrogen (attached to the asymmetric carbon atom) and the chlorine of the –COCl group may be more mobile than in the acid chloride itself. We have not investigated the product fully, but it does not exhibit the properties of a keten, although its analysis accords with that of phenyl-α-naphthylketen.

Experimental.

r-*Phenyl-α-naphthylglycollic Acid.*—Beckmann and Paul (*Annalen*, 1891, **266**, 1) obtained this acid by acting on the sodium derivative of phenyl α-naphthyl ketone with carbon dioxide, and one of us (J., 1906, **89**, 365), in the course of work on asymmetric synthesis, obtained the acid from magnesium α-naphthyl bromide and *l*-bornyl benzoylformate. The method now described is based on the lines :

$$COPh\cdot CO_2Et \longrightarrow (I)C_{10}H_7\cdot CPh(OMgBr)\cdot CO_2Et \longrightarrow$$
$$C_{10}H_7\cdot CPh(OH)\cdot CO_2Et \longrightarrow C_{10}H_7\cdot CPh(OH)\cdot CO_2H.$$

The two ketonic groups in ethyl benzoylformate are not equally prone to attack by Grignard reagents, the one to which the phenyl group is attached being very readily acted on, whereas the other in the carbethoxy group is remarkably stable (J., 1904, **85**, 1249; Roger, this vol., p. 518). No special precautions need, therefore, be observed in regulating the interaction of the ketonic ester and magnesium α-naphthyl bromide by using the latter in the quantity necessary to combine with one of the carbonyl groups only, since the magnesium complex (I) is not readily susceptible to further attack by the reagent.

Benzoylformic acid, prepared by the oxidation of mandelic acid with alkaline permanganate, was converted into its ethyl ester, which had b. p. 127°/10 mm., whereas Acree (*Amer. Chem. J.*, 1913, **50**, 391) gives 125°/9 mm.

For the preparation of the hydroxy-acid the following procedure is typical. An ethereal solution of 73 g. of ethyl benzoylformate (1 mol.) was added within 40 minutes to the Grignard reagent prepared from 134 g. of α-bromonaphthalene (slightly more than 1½ mols.). The flask was surrounded by ice, and at no time was

the reaction allowed to become vigorous. After the mixture had been warmed for 1 hour, ice and dilute sulphuric acid were added, the ethereal solution was separated, and after the expulsion of the ether the residual oil was heated with a slight excess of alcoholic potash for 2 hours. The solution was then distilled with steam to remove alcohol, naphthalene, and dinaphthyl, the residue was extracted with ether, and the aqueous solution of potassium phenyl-α-naphthylglycollate decolorised by charcoal. The acid, which is very sparingly soluble in water, was precipitated by an excess of dilute hydrochloric acid. It separated (with 2 mols. H_2O) from aqueous alcohol in prismatic needles, m. p. 112—118° (Beckmann and Paul give 108—115°). Yield: 79 g.

The anhydrous acid was obtained by crystallising the hydrated acid from benzene, from which it separated in colourless prisms, melting to a green liquid at 146—147° (Beckmann and Paul give 148°). It gives a green coloration with cold concentrated sulphuric acid * (Found in *silver* salt: Ag, 28·2. $C_{18}H_{13}O_3Ag$ requires Ag, 28·2%).

Conversion of Phenyl-α-naphthylglycollic Acid into α-Naphthyldeoxybenzoin.—A mixture of the anhydrous hydroxy-acid (54 g.) and phosphorus pentachloride (159 g.) was heated on the steam-bath for 3 hours until the evolution of hydrogen chloride was completed. Whilst still hot, the oil was poured upon crushed ice in a flat dish; it gradually hardened to a yellow solid, which was powdered under water and kept in contact with water over-night in the ice-chest. The solid was washed with ice-cold water, dried in a vacuum, and crystallised from benzene–light petroleum (b. p. 80—100°). Yield: 45 g.

Phenyl-α-naphthylchloroacetyl chloride, $C_{10}H_7{\cdot}CPhCl{\cdot}COCl$, separates from benzene and light petroleum in colourless, hexagonal plates, m. p. 155—156° (Found: Cl, 22·8. $C_{18}H_{12}OCl_2$ requires Cl, 22·5%). It is somewhat sparingly soluble in ether. It gives no coloration with cold concentrated sulphuric acid.

5 G. of the acid chloride (1 mol.) were added gradually to the Grignard reagent prepared from 17 g. of bromobenzene (6 mols.). After each addition the reaction was vigorous, the ether boiling briskly. The mixture was heated for 2 hours, and ice, ammonium chloride, and ammonia were then added. The ether was removed from the ethereal solution, and the product was distilled in steam to remove benzene and diphenyl. The residue was extracted with ether, the extract dried with anhydrous sodium sulphate, and after expulsion of the ether, the oil was dried in a vacuum for several days.

* In the colour reactions with sulphuric acid described in this paper, only a trace of the compound added was used.

The resin was then triturated with benzene–light petroleum (b. p. 40—60°); the undissolved solid (1·6 g.) was crystallised first from light petroleum and finally from aqueous alcohol; 1·1 g. of pure α-naphthyldeoxybenzoin (m. p. 109—110°), crystallising in octahedral prisms, were thus obtained (Found: C, 89·1; H, 5·7. Calc., C, 89·4; H, 5·6%). Its identity with the α-naphthyldeoxybenzoin prepared by McKenzie and Dennler (*loc. cit.*) was established by the melting point of the mixture not being depressed, and by the coloration with concentrated sulphuric acid.

Action of Magnesium Methyl Iodide on α-Naphthyldeoxybenzoin.—1·7 G. of α-naphthyldeoxybenzoin (1 mol.) were acted on by the Grignard reagent prepared from 7·5 g. of methyl iodide (10 mols.). The heating was continued for 10 hours, and the product decomposed by ice and dilute sulphuric acid.

αβ-Diphenyl-α(α-naphthyl)-propan-β-ol, $C_{10}H_7$·CHPh·CMePh·OH, separates from rectified spirit in glistening needles, m. p. 124—125° (Found: C, 88·9; H, 6·6. $C_{25}H_{22}O$ requires C, 88·7; H, 6·6%). It is readily soluble in ether, acetone, chloroform, or benzene, and moderately soluble in ethyl alcohol and hot light petroleum. It gives no coloration after 5 minutes when dissolved in cold concentrated sulphuric acid.

Action of Benzene and Aluminium Chloride on Phenyl-α-naphthylacetyl Chloride.

Phenyl-α-naphthylacetic Acid.—Phenyl-α-naphthylglycollic acid (29 g.), glacial acetic acid (100 c.c.), concentrated hydriodic acid (7·5 g.), and red phosphorus (7·5 g.) were heated together for 1 hour on the steam-bath. Addition of water to the filtered solution precipitated a gum, which solidified gradually and was then crystallised from aqueous alcohol; phenyl-α-naphthylacetic acid separated in rosettes of needles, m. p. 140—141° (Found: C, 82·2; H, 5·6. Calc., C, 82·4; H, 5·4%). Yield: 20 g. This is a much more convenient preparative method than that described by Michael and Jeanprêtre (*Ber.*, 1892, **25**, 1615), who obtained the acid (m. p. 141°) from phenyl-α-naphthylacetonitrile.

The acid is readily soluble in ether, ethyl alcohol, benzene or light petroleum, and it gives a cherry-red coloration with cold concentrated sulphuric acid.

A mixture of phenyl-α-naphthylacetic acid (19 g.) and thionyl chloride (35 g.) was heated until the evolution of hydrogen chloride ceased, and the excess of thionyl chloride was then removed in a vacuum over soda–lime. The resulting oil solidified gradually, and was then crystallised from benzene–light petroleum (b. p. 40—60°). Yield: 16 g. *Phenyl-α-naphthylacetyl chloride,* $C_{10}H_7$·CHPh·COCl,

crystallises in needles, m. p. 74·5—75·5° (Found: Cl, 12·8. $C_{18}H_{13}OCl$ requires Cl, 12·7%). It is very soluble in benzene, and sparingly soluble in light petroleum.

The acid chloride (16 g.) was heated with benzene (160 c.c.) and freshly-sublimed aluminium chloride (34 g.) for 1½ hours until the evolution of hydrogen chloride was completed. The mixture was decomposed by ice and hydrochloric acid, the benzene layer shaken with an aqueous solution of sodium bicarbonate, and the benzene removed by steam. The resulting oil solidified slowly, and the solid (7 g.) was crystallised twice from ether–light petroleum (b. p. 80—100°), and finally from methyl alcohol. The resulting *compound*, which did not contain chlorine, crystallised in rectangular plates, m. p. 115·5—116·5° (Found: C, 88·2; H, 5·1. $C_{18}H_{12}O$ requires C, 88·5; H, 5·0%). It is readily soluble in acetone or chloroform; sparingly soluble in cold methyl alcohol or ethyl alcohol, but readily soluble on heating; sparingly soluble in boiling light petroleum (b. p. 40—60°); when heated with aqueous *N*-caustic soda, an intense magenta coloration appears. It does not decolorise an alcoholic solution of bromine. The analytical figures and the melting point did not agree with those required for α-naphthyldeoxybenzoin, nor did the substance possess the properties of the latter. With cold concentrated sulphuric acid it gave an intense yellow coloration, and when mixed either with α-naphthyldeoxybenzoin or with diphenylacetonaphthone the melting point was in each case depressed.

The above compound was not the only product of the Friedel and Crafts reaction, since from the gums resulting from the several preparations a solid separating from aqueous alcohol in prisms, m. p. 240—241°, was isolated, and this gave with cold concentrated sulphuric acid a brown coloration changing to olive-green.

Action of Grignard Reagents on Phenyl-α-naphthylchloroacetyl Chloride.

Phenyl-α-naphthylacetone.—5 G. of phenyl-α-naphthylchloroacetyl chloride (1 mol.) were added gradually to the Grignard reagent prepared from 18 g. of methyl iodide (7 mols.). The ether boiled briskly and a green coloration was noted. After heating for 3 hours, the mixture was decomposed by ice, ammonium chloride, and ammonia, and the ether distilled from the ethereal solution. The resulting oil (4 g.) was crystallised from aqueous alcohol.

Phenyl-α-naphthylacetone, $C_{10}H_7 \cdot CHPh \cdot COMe$, separates from aqueous alcohol in square plates, m. p. 84·5—85° (Found: C, 87·2; H, 6·4. $C_{19}H_{16}O$ requires C, 87·6; H, 6·2%). Yield: 1 g. It is very insoluble in water, and readily soluble in ethyl alcohol, benzene,

chloroform, acetone, or ethyl acetate. It gives a crimson coloration with cold concentrated sulphuric acid, and no coloration with alcoholic ferric chloride.

The ketone was disrupted by heating with alcoholic potash for 4 hours, when phenyl-α-naphthylmethane and acetic acid were identified as the products of the action :

$$\begin{matrix} C_{10}H_7\cdot CHPh\text{–}\vdots\text{–}COMe \\ H\text{–}\vdots\text{–}OH \end{matrix}$$

Phenyl-α-naphthylacetonaphthone.—10 G. of phenyl-α-naphthylchloroacetyl chloride (1 mol.) were added during 20 minutes to the Grignard reagent prepared from 40 g. of α-bromonaphthalene (6 mols.). The action was brisk, and the solution became yellow. After 2½ hours' heating, decomposition was effected by ice and dilute sulphuric acid, the ether was expelled, and the naphthalene and dinaphthyl partly removed by steam distillation. The aqueous-alcoholic solution of the resulting oil was decolorised with charcoal, and from the filtrate some dinaphthyl first separated. The latter was removed, and the crude ketone (2 g.) separated on concentration of the solution. It was purified by further crystallisation from aqueous alcohol.

Phenyl-α-naphthylacetonaphthone, $C_{10}H_7\cdot CHPh\cdot CO\cdot C_{10}H_7$, separates from light petroleum in prisms, m. p. 125—126° (Found : C, 90·0; H, 5·6. $C_{28}H_{20}O$ requires C, 90·3; H, 5·4%). It gives an orange-yellow coloration with cold concentrated sulphuric acid.

α-Naphthoic acid was isolated from the solution obtained by heating the ketone with alcoholic potash for 6 hours.

Phenyl-α-naphthylmethyl p-*Tolyl Ketone.*—Phenyl-α-naphthylchloroacetyl chloride (5 g.) was gradually added to the Grignard reagent prepared from *p*-bromotoluene (20 g.). The solution became green, and after the vigorous action had subsided, the mixture was heated for 5 hours and decomposed by ice, ammonium chloride, and ammonia. The residual oil from which the bulk of the ditolyl had been removed by steam was extracted with ether. When the ethereal solution was concentrated, 2·4 g. of the nearly pure ketone separated, and this was crystallised from aqueous alcohol.

Phenyl-α-naphthylmethyl p-*tolyl ketone*, $C_{10}H_7\cdot CHPh\cdot CO\cdot C_7H_7$, separates from aqueous alcohol, or from benzene–light petroleum (b. p. 60—80°) in prisms, m. p. 141—142° (Found : C, 89·2; H, 6·1. $C_{25}H_{20}O$ requires C, 89·2; H, 6·0%). With cold concentrated sulphuric acid it gives a yellow coloration. It is readily soluble in benzene or ethyl alcohol, and sparingly soluble in light petroleum.

When heated with alcoholic potash for $3\frac{1}{2}$ hours, it underwent disruption according to the scheme:

$$C_{10}H_7\cdot CHPh\text{–}\overset{|}{\underset{|}{}}\text{–}CO\cdot C_6H_4Me$$
$$H\text{–}\overset{|}{\underset{|}{}}\text{–}OH$$

phenyl-α-naphthylmethane and *p*-toluic acid were isolated.

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CCCXLIX.—*Olefinic Terpene Ketones from the Volatile Oil of Flowering* Tagetes glandulifera. *Part I.*

By THOMAS GILBERT HENRY JONES and FRANK BERRY SMITH.

Tagetes glandulifera (n.o. *Compositæ*), an annual native to South America, is a conspicuous floral feature in portions of coastal Queensland, attracting attention by reason of its powerful and somewhat unpleasant perfume at the flowering period. The flowers are borne in dense terminal panicles, and the calyces are distinguished by abundant and clearly visible oil glands. In view of characters, somewhat unusual in essential oils of *Compositæ*, displayed by the flower oil of *T. petula* (Schimmel and Co. Rep., November, 1908, p. 141; April, 1909, p. 87) and by that of *T. annisata* (Zelada, thr. *Chem. Abs.* 1922, 4011), the volatile oil yielded by the flowers of *T. glandulifera* was deemed to merit investigation; and to that end quantities of the flowering plants were gathered in the neighbourhood of Brisbane in the autumns of 1923 and 1924, and steam distilled.

The volatile oil of flowering *T. glandulifera* contains, in addition to terpenic constituents, ocimene (30%) and *d*-limonene (3%), two closely related and hitherto unrecorded ketones of the olefine terpene series, comprising respectively 5—10 and 50—60% of the oil and having molecular compositions $C_{10}H_{18}O$ and $C_{10}H_{16}O$. The behaviour and properties of these ketones indicate that they are *γη-dimethyl-Δ$^{\alpha}$-octen-ε-one*, $CH_2{:}CH\cdot CHMe\cdot CH_2\cdot CO\cdot CH_2\cdot CHMe_2$ and *η-methyl-γ-methylene-Δ$^{\alpha}$-octen-ε-one*,

$$CH_2{:}CH\cdot C(:CH_2)\cdot CH_2\cdot CO\cdot CH_2\cdot CHMe_2,$$

respectively. The name *tagetone* is proposed for the latter ketone, which is the principal and characteristic constituent of the volatile oil. From our observation of a small quantity of the volatile oil of the flowers of *T. petula* and from the recorded characters of that

oil, it appears probable that it also contains tagetone as a main constituent.

γη-Dimethyl-Δ$^{\alpha}$-octen-ε-one, isolated from the lower-boiling fractions and purified by regeneration from the *semicarbazone* (m. p. 92·5°), is a colourless, mobile liquid boiling at 185°/760 mm. and possessing small but distinct optical activity. It forms a liquid *dibromide*, and is reduced by hydrogen in presence of a catalyst to a saturated ketone, $C_{10}H_{20}O$ (*γη-dimethyloctan-ε-one*).

Oxidation of γη-dimethyl-Δ$^{\alpha}$-octen-ε-one with potassium permanganate in acetone at 0° gave as main product a ketonic acid, $C_9H_{16}O_3$ (β-iso*valeryl-α-methylpropionic acid*), together with smaller amounts of *iso*valeric and formic acids. The keto-acid had the characteristics of a γ-ketonic acid, and was optically active, with small rotation opposite in direction to that of the parent ketone.

The keto-acid, of which relatively little was available for oxidation experiments, was attacked slowly by permanganate in acetone at 30°, the greater portion being recovered; the products were *iso*valeric and acetic acids together with a small quantity of solid acid, presumably dibasic, insufficient for identification. With aqueous alkaline permanganate, oxidation proceeded readily at 0°, considerably more of the oxidant being consumed than required for the primary products theoretically indicated; there were isolated acetic acid in large amount, one molecular proportion of oxalic acid, and a smaller quantity of *iso*valeric acid. With chromic acid, the product consisted mainly of acetic acid, although *iso*valeric acid was obtained and a small amount of methylsuccinic acid.

Oxidation of the saturated ketone (γη-dimethyloctan-ε-one) with 3% alkaline aqueous permanganate at the ordinary temperature (25—30°) yielded α-methylbutyric, acetic, and oxalic acids; but no *iso*valeric acid. With chromic acid, the products were β-methylvaleric, α-methylbutyric, and acetic acids. The formation of these acids on oxidation, in conjunction with the production of *iso*valeric acid from the unsaturated ketone, shows that the saturated ketone is γη-dimethyloctan-ε-one, $CH_3{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CHMe_2$.

Tagetone is a light yellow liquid with a peculiar and characteristic odour, and comprises the highest-boiling fraction of the volatile oil. It is remarkably prone to alteration; readily absorbs oxygen, and polymerises slowly at the ordinary temperature and rapidly on heating, the change being almost complete at the boiling point (210°/760 mm.). On heating with dilute acids and dilute aqueous alkali, indefinite resinous substances are formed. It reacts vigorously with sodium on warming, a red, resinous mass being produced; a trace of sodium ethoxide imparts a deep red colour. Sodium slowly reacts with the substance dissolved in anhydrous ether, a red

sodium salt being produced. In reaction with bromine four atoms are added to the ketone, but hydrogen bromide is immediately evolved; a definite bromide could not be isolated.

Crystalline derivatives of tagetone were not obtained. The product of reaction with semicarbazide was resinous and uncrystallisable; the readily formed *oxime* is liquid.

The ketonic character of tagetone was fully established by its almost quantitative reduction, by hydrogen in presence of platinum black, to a saturated ketone, the identity of which with $\gamma\eta$-dimethyloctan-ε-one was proved by comparison of the physical constants, products of oxidation, and the semicarbazones, which melted each separately and in admixture sharply at 91·5°.

Reduction of tagetone with sodium in moist ether produced mainly a *substance*, $C_{10}H_{18}O$; another product was a stable *pinacol*, $C_{20}H_{34}O_2$, which was also obtained by electrolytic reduction of tagetone in acid alcoholic solution with a platinum or nickel cathode.

Oxidation of tagetone with aqueous alkaline permanganate produced principally *iso*valeric acid in almost quantitative yield and oxalic acid in one molecular proportion.

Of the possible alternative formulæ assignable to tagetone, namely, those comprising the systems $\cdot CO\cdot CH_2\cdot C(:CH_2)\cdot CH:CH_2$ and $\cdot CO\cdot CH:CMe\cdot CH:CH_2$, the former alone seems to account for the behaviour of the substance on oxidation, and the reaction with sodium and obvious salt-formation. The tendency to assume the enolic form which comprises the doubly conjugated system

$$\cdot C(OH):CH\cdot C(:CH_2)\cdot CH:CH_2$$

affords a ready explanation of the instability and proneness of tagetone to polymeric change.

Neither $\gamma\eta$-dimethyloctan-ε-one, derived by reduction of the natural ketones and affording the key to their structure, nor β-*iso*valeryl-α-methylpropionic acid, obtained as primary product of oxidation of $\gamma\eta$-dimethyl-Δ^{α}-octen-ε-one, has, apparently, been previously described. The apparent anomaly in deportment of the former towards aqueous alkaline potassium permanganate, *iso*valeric acid being wholly absent from among the products of oxidation, is probably to be attributed to rupture of the molecule at the 7-carbon atom (compare Crossley and Perkin, J., 1898, **73**, 21), oxalic acid being thereby produced. The synthesis of these substances is being undertaken.

The position of the carbonyl group in the molecules of these new natural ketones corresponds to that of the same group in the ruptured menthone ring. For the purpose of studying ring formation and continuing, generally, the examination of these olefinic ketones, a further seasonal supply of oil is awaited.

Experimental.

The volatile oil of flowering *T. glandulifera* is a bright yellow, somewhat mobile liquid having the powerful cloying odour of the crushed flowers, reminiscent of the principal constituent and of olefinic terpenes. It slowly resinified on keeping, and on exposure left a tacky, resinous residue.

The amount secured from approximately 1½ tons of flowering plants, it being impracticable on the large scale to separate the flowers, was 3·5 kilo., equivalent to 0·5%. A yield of 1% was obtained in a small distillation of floral portions alone. The recovery of volatile oil from the plants prior to flowering was extremely small; the difference in constants of oils distilled from whole plants and floral portions would, however, indicate that at flowering the proportion of terpenic constituents is considerably augmented by the leaves, and that the seat of the ketones is mainly, if not exclusively, the floral parts.

Evidence of considerable resinification during distillation was seen in the viscid yellow resin coating the still-head and still residues.

The constants recorded for the oils were the following: Oil from flowering plants, $d^{15·5°}$ 0·8638; $n_D^{20°}$ 1·4820; $[\alpha]_D + 4°$; acid value 2; acetyl value 33.

Oil from flowers, $d^{15·5°}$ 0·8743; $n_D^{20°}$ 1·4870; $[\alpha]_D + 2·5°$; acid value and acetyl value not determined.

The usual reagents extracting practically nothing, the oil (3,800 c.c.) was fractionally distilled at 3—4 mm. through a 3-section Young fractionating column, a trap cooled by liquid ammonia being interposed between the pump and receivers. The following fractions were collected:

		$d^{15·5°}$.	$n_D^{20°}$.	$[\alpha]_D$.
0—45°	1,200 c.c.	0·8285	1·4710	+9·1°
45—50	400	0·8544	1·4710	+2
50—58	325	0·8671	1·4770	+0·6
58—65	1,150	0·8803	1·4850	+0·3
Ammonia trap	50			

Loss by resinification 675 c.c. equiv. to 18%.

Repeated refractionation, first at 3—4 mm. to reduce as far as possible loss by resinification, eventually yielded three main, with small intermediate fractions.

		$d^{15·5°}$.	$n_D^{20°}$.	$[\alpha]_D$.
(*a*) 72—75°/24 mm.	800 c.c.	0·8143	1·4695	+15°
(*b*) 85—90°/24 mm.	150	0·8420	1·4523	+ 1
(*c*) 55—65°/3 mm.	1,300	0·8804	1·4890	—

Fraction (a) was mainly terpenic; the somewhat low refractive index of (b) suggested the presence of a ketone or ketones; while

fraction (c) was apparently practically homogeneous and comprised the main constituent of the oil.

Fraction (a) was twice treated with semicarbazide acetate in alcohol for removal of any ketone present, the solution was neutralised, and the terpenes were distilled in steam. A quantity of crystalline semicarbazone remaining was digested with dilute sulphuric acid, and the regenerated ketone added to fraction (b).

The distilled terpenes then had $\alpha = +13°$ ($l = 1$), and for separation of the active constituent were submitted to exhaustive refractionation under the conditions found most effective, namely, a Young 3-section column and 3 mm. pressure.* There were thus obtained a head fraction (50 c.c.) showing $\alpha = +65°$ ($l = 1$), and the bulk ($\alpha = +3°$; $l = 1$).

Identification of d-*Limonene and Ocimene.*—The head fraction was distilled from sodium and finally fractionated at atmospheric pressure; it was then collected mainly at 173—178° with constants: $d^{15·5°}$ 0·8346; $[\alpha]_D + 88°$; iodine value 410 (equiv. to 4·3 atoms) (Found: C, 88·1; H, 11·6%).

The presence of *d*-limonene (admixed still with 16% of ocimene), suspected from the constants, was confirmed by preparation of the tetrabromide (m. p. 104°).

The large subfraction, distilled from sodium, had constants $d^{15·5°}$ 0·8058; $n_D^{20°}$ 1·4855; b. p. 71—72°/15 mm., 84—85°/30 mm. (Found: C, 87·9; H, 11·6%).

Identity with ocimene was established by (*a*) reduction by hydrogen in presence of platinum black to dimethyloctane (b. p. 158—159°/760 mm.; $d^{15·5°}$ 0·7406; $n_D^{20°}$ 1·4091; (*b*) conversion into *allo*ocimene (b. p. 185°/760 mm.; $d^{15·5°}$ 0·818; $n_D^{20°}$ 1·519; (*c*) reduction by sodium in alcohol to dihydroocimene, whence was prepared the crystalline tetrabromide (m. p. 88°).

Isolation and Characterisation of $\gamma\eta$-*Dimethyl-*Δ^{α}-*octen-*ε-*one.*

In order completely to separate from associated terpene, the ketone of fraction (*b*), supplemented by ketone regained from fraction (*a*), was converted into semicarbazone. This was recrystallised several times from dilute alcohol, and the ketone regenerated by warming with 20% oxalic acid solution and distilled under reduced pressure. The following constants were recorded: $d^{15·5°}$ 0·8354, $n_D^{20°}$ 1·4295, $[\alpha]_D + 1·5°$; b. p. 185—186°/760 mm.,

* Despite the higher boiling point at the ordinary pressure, *d*-limonene boils slightly below ocimene at 3—4 mm. At 30 mm., the boiling points apparently coinciding, no separation by fractionation was practicable. Separation at ordinary pressure can be slowly accomplished owing to the gradual production of *allo*ocimene, b. p. 185°.

88—89°/30 mm. (Found: C, 77·7; H, 11·5. $C_{10}H_{18}O$ requires C, 77·9; H, 11·7%). The small optical rotation was unaffected by further recrystallisation of the semicarbazone.

The ketone combined neither with sodium sulphite nor bisulphite, nor did it react with Schiff's reagent or ammoniacal silver. It was unaffected by boiling under reflux for several hours with 20% sulphuric acid.

The *semicarbazone* crystallised from alcohol in needles, m. p. 92·5° (Found: C, 62·2; H, 9·9; N, 19·6. $C_{11}H_{21}ON_3$ requires C, 62·5; H, 9·9; N, 19·9%). The *oxime*, prepared by the usual method, had b. p. 222°/760 mm.; $d^{15·5°}$ 0·8778; $[\alpha]_D$ + 2·4° (Found: N, 8·1. $C_{10}H_{19}ON$ requires N, 8·3%).

γη-Dimethyl-Δ$^{\alpha}$-octen-ε-ol.—To 10 g. of the ketone in absolute alcohol boiling under reflux was added in fragments twice the theoretical amount of sodium. By dilution with water and extraction with ether an alcohol was obtained, b. p. 92°/20 mm., $d^{15·5°}$ 0·8305; $n_D^{20°}$ 1·440; $[\alpha]_D$ + 1·75° (Found: C, 76·7; H, 12·6. $C_{10}H_{20}O$ requires C, 76·9; H, 12·8%). A crystalline phenylurethane was not obtained.

Reduction of γη-Dimethyl-Δ$^{\alpha}$-octen-ε-one to γη-Dimethyloctan-ε-one.—The ketone (20 g.) was repeatedly volatilised in purified hydrogen over a nickel catalyst on pumice in a U-tube at 180° until the product failed to decolorise bromine. Alternatively, reduction was effected at the ordinary temperature with platinum black as catalyst, suspended in a well-shaken ethereal solution of the ketone. The saturated *ketone* had b. p. 187—188°/760 mm.; $d^{15·5°}$ 0·8201; $n_D^{20°}$ 1·4205; $[\alpha]_D$ — 1·5°.

The *semicarbazone* crystallised from dilute alcohol in needles, m. p. 91·5° (Found: C, 61·5; H, 10·8; N, 19·6. $C_{11}H_{23}ON_3$ requires C, 61·9; H, 10·8; N, 19·7%). The *oxime* had b. p. 224—225°/760 mm.; $d^{15·5°}$ 0·8419; $n_D^{20°}$ 1·4338 (Found: N, 8·0. $C_{10}H_{21}ON$ requires N, 8·2%).

γη-Dimethyloctan-ε-ol.—By the action of sodium on γη-dimethyloctan-ε-one in boiling absolute alcohol was produced an *alcohol* of notably pleasant odour with constants $d^{15·5°}$ 0·8230; $n_D^{20°}$ 1·4270; b. p. 195°/760 mm. (Found: C, 75·7; H, 13·7. $C_{10}H_{22}O$ requires C, 75·9; H, 13·9%). A crystalline phenylurethane was not obtained.

Oxidation Products of γη-Dimethyl-Δ$^{\alpha}$-octen-ε-one. Isolation of a Ketonic Acid, $C_9H_{16}O_3$.—To 25 g. of the ketone in 200 c.c. of acetone, cooled in ice, was added fine-sieved potassium permanganate (120 g.); reaction then appeared complete. The aqueous saline solution, obtained by thorough leaching of the precipitated oxide of manganese removed by filtration and washed with acetone, was

concentrated to small bulk and acidified. The liberated acids were extracted with ether, finally in a continuous extractor, and after esterification with ethyl alcohol were resolved by fractional distillation into the following fractions: (*a*) below 100°, principally ethyl formate and acetate; (*b*) 100—130°, principally ethyl *iso*-valerate, *iso*valeric acid being identified by the character and analysis of the silver salt, and by preparation of the anilide (m. p. 110—111°); (*c*) 130—180°/760 mm., a mixture of (*b*) and (*d*); (*d*) 126—130°/25 mm. This was refractionated, when the greater portion boiled constantly at 127°/25 mm. (Found: C, 66·2; H, 10·1. $C_{11}H_{20}O_3$ requires C, 66·0; H, 10·0%).

The ester reacted with semicarbazide and was evidently the ester of a ketonic acid, which, from absence of colour reaction with alcoholic ferric chloride and its stability towards heat, was judged to be a γ-ketonic acid.

The γ-ketonic acid, β-iso*valeryl*-α-*methylpropionic acid*, was subsequently prepared in larger yield by oxidation of $\gamma\eta$-dimethyl-Δ^{α}-octen-ε-one in acetone strictly at 0° with the theoretical amount of permanganate, and separation as principal product from the extracted acids by fractional distillation under reduced pressure without previous esterification. It solidified below 25°, crystallising in long needles, and melted sharply at that temperature: b. p. 169—171°/25 mm.; $\alpha_D^{27^\circ} - 2{\cdot}1°$ ($l = 1$) (Found: C, 62·3; H, 9·3. $C_9H_{16}O_3$ requires C, 62·7; H, 9·3%).

The *semicarbazone*, crystallised from water, melted at 165° (Found: C, 52·5; H, 8·4; N, 18·3. $C_{10}H_{19}O_3N_3$ requires C, 52·4; H, 8·3; N, 18·3%).

The semicarbazone of the ethyl ester (b. p. 127°/25 mm.), crystallised from alcohol, melted at 122°.

Oxidation of the γ-Ketonic Acid.—(*a*) To 5 g. of the acid was added aqueous alkaline 2% permanganate (28 g., equiv. to 9 oxygen atoms) until reaction was complete, the whole being kept cool in an ice-bath. The products isolated were *iso*valeric acid in small amount, oxalic acid (1 mol.), and a large amount of acetic acid; no dibasic acid other than oxalic could be detected. (*b*) The acid in acetone at 30° was treated with finely sieved potassium permanganate. The products identified were *iso*valeric and acetic acids. By prolonged extraction with ether of the still-liquor after removal of the volatile acids, a trace of crystalline acid was obtained insufficient for identification. (*c*) The acid (5 g.) was refluxed for 4 hours with 15 g. of potassium dichromate and 5 c.c. of concentrated sulphuric acid in 75 c.c. of water The products isolated by distillation were *iso*valeric acid in small amount and acetic acid, and by subsequent ether extraction methylsuccinic acid (0·15 g.), m. p. 112° after

recrystallisation from ether (Found: C, 45·4; H, 6·1. Calc., C, 45·4; H, 6·1%).

Oxidation of γη-Dimethyloctan-ε-one with Chromic Acid.—The largest relative yield of volatile acids was obtained by the following procedure. In each of three experiments, 10 g. of the ketone were refluxed during 12 hours with 10 g. of potassium dichromate and 8 c.c. of concentrated sulphuric acid in 65 c.c. of water; on isolation, about half the ketone was recovered unchanged and volatile acids equivalent to 2·0 g. of sodium hydroxide were distilled in steam. The distillates were digested with moist silver oxide and the relatively soluble silver salts were obtained after repeated recrystallisations in fractions containing respectively in order of increasing solubility (*a*) 48·4, (*b*) 51·7, (*c*) 62·5% of silver.

The identity of (*a*) with silver β-methylvalerate was established by preparation from the regenerated acid of β-methylvaleranilide, m. p. 88° (J., 1895, **67**, 268); that of the second acid (*b*), evidently the principal product, with *d*-methylbutyric acid by means of the amide, m. p. 110°, and of an anilide, prepared through the acid chloride and crystallised from light petroleum, which melted, alone or mixed with an authentic specimen, at 104·5°. Silver *d*-methylbutyrate was readily distinguished from the silver salts of *n*- and *iso*-valeric acids by its greater solubility and its crystalline form. Fraction (*c*) was essentially silver acetate.

Oxidation of γη-Dimethyloctan-ε-one with Potassium Permanganate.—A greater yield of volatile acids was obtained with potassium permanganate as oxidant. The ketone (10 g.) was slowly oxidised when shaken at room temperature with 3% alkaline permanganate; for practically complete oxidation, 60 g. of potassium permanganate (equiv. to 10 oxygen atoms) were required. The filtrate and washings from the oxide of manganese were concentrated and acidified, and the volatile acids distilled in steam were equivalent to 4·1 g. of sodium hydroxide. The residual liquor was exhaustively extracted with ether, but only oxalic acid was recovered and identified. The readily soluble volatile acids were partly separated from the acetic acid in the distillate by shaking with ether, and were converted into silver salts; by fractional crystallisation, silver α-methylbutyrate (Found: Ag, 51·7%) was obtained which was identified by preparation of the anilide (m. p. 104·5°).

Tagetone (*η-Methyl-γ-methylene-Δ$^{\alpha}$-octen-ε-one*).

The highest-boiling fraction (*c*) of the oil (p. 2533) was further fractionated; even at 3—4 mm. considerable resinification occurred, and the bulk was collected at 62°.

The constants of the pale yellow liquid, the colour of which per-

sisted through successive redistillations and therefore appeared to be constitutive, were : $d^{15\cdot5°}$ 0·8803 ; $n_D^{20°}$ 1·4895 ; b. p. 102°/30 mm., *ca.* 205—210°/760 mm. (Found : C, 78·8 ; H, 10·5. $C_{10}H_{16}O$ requires C, 78·9 ; H, 10·5%). The molecular refraction is 49·9 (Calc. for $C_{10}H_{16}O$ with two ethylenic linkings, 48·5).

Tagetone oxime was obtained in reasonable yield as a comparatively stable liquid of unpleasant odour, b. p. 126°/25 mm., by heating tagetone with the theoretical quantities of hydroxylamine hydrochloride and sodium bicarbonate : $d^{15\cdot5°}$ 0·9207 ; $n_D^{20°}$ 1·4820 (Found : C, 71·9 ; H, 10·2 ; N, 8·2. $C_{10}H_{17}ON$ requires C, 71·8 ; H, 10·2 ; N, 8·4%).

Reduction of Tagetone to γη-Dimethyloctan-ε-one.—Pure dry hydrogen was rapidly absorbed when it was passed into well-shaken dry ether (100 c.c.) containing 30 g. of tagetone and 5 g. of platinum black (prepared by Loew's method) ; passage of the gas was continued until the product no longer decolorised bromine (about 5 hours). The saturated ketone produced (yield almost quantitative), after redistillation, had constants, b. p. 187—188°/760 mm., $d^{15\cdot5°}$ 0·8198, $n_D^{20°}$ 1·4205 (semicarbazone, m. p. 91·5°), identical with those of γη-dimethyloctan-ε-one and gave the same products on oxidation with alkaline potassium permanganate.

Reduction of Tagetone in Ether by Sodium.—Reduction of tagetone by sodium and absolute alcohol produced indefinite, red, resinous substances. Isolable products were obtained by reduction in moist ether.

To a solution of 40 g. of tagetone in 200 c.c. of ether, floating on concentrated aqueous sodium bicarbonate, sodium was added in small fragments ; water was occasionally added to promote dissolution of the sodium, and the reaction was modified, as necessary, by immersing the flask in cold water. The product, on fractionation, gave (*a*) a *substance*, b. p. 197°/760 mm., $d^{15\cdot5°}$ 0·8524, $n_D^{20°}$ 1·4490 (Found : C, 77·6 ; H, 11·6. $C_{10}H_{18}O$ requires C, 77·9 ; H, 11·7%), and (*b*) the pinacol, b. p. 183°/4 mm., described below.

Electrolytic Reduction of Tagetone.—The reduction was effected in a divided cell, the anode compartment containing a platinum spiral and 10% sulphuric acid. The cathode liquid was composed of 20 c.c. of tagetone, 70 c.c. of 95% alcohol, 10 c.c. of 10% sulphuric acid, and 0·4 g. of nickel sulphate. The cathode was an activated nickel foil cylinder, etched by nitric acid, of surface area 2·2 cm.^{2} (alternatively, a platinum dish was employed). The system was cooled in running water. The current density was maintained at 3·5—4 amp./cm.^{2} by addition, as required, of 10% sulphuric acid to the cathode liquid. The *E.M.F.* was 8—12 volts throughout.

When reduction was considered complete (27 hours), the cathode

liquid was poured into water. The separated product, after distillation, had $d^{15\cdot5°}$ 0·9258, $n_D^{20°}$ 1·4820, b. p. 183°/4 mm. (Found : C, 78·2; H, 11·0. $C_{20}H_{34}O_2$ requires C, 78·4; H, 11·1%). The iodine value (328) indicated four ethylenic linkings. Evidently a pinacol, the substance was comparatively stable to heat, showing no tendency to resinification or decomposition on distillation at 4 mm. pressure.

Oxidation of Tagetone.—The ketone (50 g.) was gradually treated in the cold with 350 g. of potassium permanganate in 2% aqueous alkaline solution; oxidation then appeared complete. After filtration from precipitated oxide of manganese and concentration and acidification of the filtrate, the volatile acids were distilled in steam. They were recovered in good yield and converted into ethyl esters, the greater portion of which distilled at 130—132°/760 mm. and was identified as ethyl *iso*valerate by conversion into *iso*valeranilide (m. p. 111°); a small lower fraction indicated some acetic acid.

Examination of the non-volatile acid extracted from the residual liquor by ether revealed only oxalic acid, determined in a small-scale quantitative oxidation as equivalent to one molecule.

Oxidation of the ketone in acetone solution with permanganate gave as principal product *iso*valeric acid, with oxalic acid, but no trace of a ketonic acid.

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CCCL.—*The Isomerism of the Styryl Alkyl Ketones. Part II. The Isomerism of the Homologues of 2-Hydroxystyryl, and of 3-Methoxy-4-hydroxystyryl Methyl Ketones.*

By ALEXANDER MCGOOKIN and DONALD JAMES SINCLAIR.

THE yellow form of 2-hydroxystyryl ethyl ketone, stated by Decker and Fellenberg (*Annalen*, 1908, **364**, 24) to melt at 101°, has m. p. 116° when pure. The colourless modification has the same m. p. (Auwers and Voss, *Ber.*, 1909, **42**, 4423, 118—119°). The two substances are stereoisomerides analogous to those of 2-hydroxystyryl methyl ketone (Part I, J., 1924, **125**, 2099). Again the yellow form is labile, and is even more readily transformed into the colourless modification than is the yellow form of the lower homologue.

As stated by Decker and Fellenberg (*loc. cit.*), when salicylaldehyde is condensed with methyl ethyl ketone a small quantity of

a yellow, crystalline substance—A—of m. p. 246—247° is also produced. This compound is not a distyryl ketone (Part I), for, although the methylene group of 2-hydroxystyryl ethyl ketone is capable of condensing with aldehydes in the presence of acids, it has been shown, by attempted condensations under varying conditions, that it is inert towards alkaline condensing agents.

Although the structure of the compound A has not yet been elucidated, the authors have proved, by analyses of the substance itself and of certain of its derivatives, that it cannot have the formula $C_{22}H_{22}O_3$ suggested for it by Decker and Fellenberg (*loc. cit.*).

Whereas the rapid development of a red coloration when the yellow isomeride of 2-hydroxystyryl methyl ketone is treated with aqueous sodium hydroxide was shown to be due to the formation of the sodium salt of 2 : 2′-dihydroxydistyryl ketone (Part I), such a reaction is obviously impossible in the case of the next higher homologue. Confirming this conclusion, both isomerides of 2-hydroxystyryl ethyl ketone give yellow solutions when treated with alkali, which, however, turn red on standing for 2 weeks on account of the slow production of the sodium salt of the compound A.

Harries and Busse (*Ber.*, 1896, **29**, 376) and Auwers and Voss (*loc. cit.*) describe 2-hydroxystyryl *n*-propyl ketone as a crystalline solid melting at 116°, but make no mention of its colour. Yellow and colourless forms have now been prepared, both of which melt at 113°. The yellow isomeride is again the unstable variety and can readily be isomerised by the usual methods (Part I). Both modifications, moreover, yield yellow alkaline solutions; these develop the usual red colour when kept for four weeks, but the amount of red sodium salt produced is too minute to be isolated.

By condensation in the usual manner 2-hydroxystyryl *n*-hexyl ketone also has been obtained in yellow and colourless forms, each melting at 102—103°. The yellow isomeride is exceedingly unstable and isomerises even in the dry state. Both forms give yellow solutions in alkali which redden after three months' exposure, but again the isolation of the red sodium salt produced is impossible on account of the small quantity formed.

A comparison of the properties of the 2-hydroxystyryl alkyl ketones indicates that the stability of the yellow isomeride decreases, and the resistance of the molecule to fission by alkaline reagents increases, with increasing molecular weight.

In Part I, it was mentioned that yellow and colourless isomerides of 3-methoxy-4-hydroxystyryl methyl ketone had been obtained. The ethyl and *n*-propyl homologues of this series have now been prepared, each in two forms—yellow and colourless—having

identical melting points. Unlike 3-methoxy-4-hydroxystyryl methyl ketone, which rapidly develops a red coloration in presence of alkali, these homologues only do so on long standing. Since the development of a red coloration is dependent on the fission of the molecule (Part I), it appears that the higher homologues in this series are also the most stable. Moreover, the 3-methoxy-4-hydroxystyryl alkyl ketones resemble the 2-hydroxy-compounds in the decreasing stability of the yellow isomerides with increasing molecular weight.

Throughout the entire series of hydroxystyryl ketones so far examined, each pair of isomers invariably has the same melting point, which is doubtless due to one form changing into the other at, or below, the melting point of the latter. Other isomeric, unsaturated ketones have been described which do not exhibit this peculiar property (compare Bodforss, *Ber.*, 1916, **49**, 2802; Dilthey and Radmacher, *Ber.*, 1925, **58**, 361).

During the preparation of the isomeric hydroxystyryl alkyl ketones it was often observed that the white isomeride has the property of "seeding" the yellow form so that the latter cannot afterwards be prepared in the same atmosphere or by the same experimenter (compare McKenzie and Roger, J., 1924, **125**, 846; Dilthey and Radmacher, *loc. cit.*).

The authors desire to correct a statement of Vavon and Faillebin (*Compt. rend.*, 1919, **169**, 65) that the yellow modification of 3:4-methylenedioxystyryl methyl ketone described by Haber (*Ber.*, 1891, **24**, 617) is an impure form of the colourless compound and is not its stereoisomeride. The existence of two distinct isomerides of this compound has been definitely established and quantitatively confirmed by solubility measurements. Similar data have been obtained in the case of 3-methoxy-4-hydroxystyryl methyl ketone, the isomerides of which have previously been described (Part I).

Since carbon dioxide is generally employed to precipitate these ketones from their alkaline solutions, it might be thought that both forms are identical and that the yellow colour of the one is due to the presence of a trace of alkali. Such, however, is not the case, since each yellow modification can be isolated from its alkaline solution by means of dilute acids.

Finally, all the hydroxystyryl ketones so far investigated are coloured crimson by boiling, concentrated hydrochloric acid, the yellow isomeride more rapidly than the colourless modification. On this account it was originally thought that the yellow form had the *cis*-configuration (Part I). As, however, similar changes have been observed in the case of hydroxystyryl ketones incapable of pyrylium salt formation, such a view cannot be maintained.

Experimental.

2-Hydroxystyryl Ethyl Ketone.—A solution of salicylaldehyde (50 g.) in aqueous sodium hydroxide (500 c.c. of 10%) rapidly became dark red after addition of alcohol (50 c.c.) and methyl ethyl ketone (10 g.). The long, yellow needles of the sodium salt of the ketone deposited after 24 hours were dissolved in water and acidified with dilute acid; the free ketone produced crystallised from benzene in colourless needles, m. p. 116° (Found: C, 74·9; H, 6·9. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·8%). If excess of 10% alkali and alcohol be employed, no sodium salt separates from the condensation mixture and on precipitation with carbon dioxide the yellow isomeride is obtained which crystallises from cyanoacetic ester in yellow needles, m. p. 116°. Addition of a trace of dilute acid to a boiling solution of the yellow form caused isomerisation (Found: C, 74·9; H, 6·7%).

Compound A was obtained in yellow needles (m. p. 246—247°) by Decker and Fellenberg's method (*loc. cit.*). It dissolved in aqueous alkali to yield a red solution of its salt (Found: C, 77·9, 78·1; H, 6·6, 6·6. Decker and Fellenberg found C, 78·1; H, 6·5%, and none of these figures agrees with the formula $C_{22}H_{22}O_3$ suggested by them, which requires C, 79·0; H, 6·5%).

The Acetyl Derivative of Compound A, prepared in the usual way, formed colourless needles, m. p. 182°, which were soluble in alcohol and ethyl acetate but insoluble in alkali (Found: C, 73·9; H, 6·3; $CH_3{\cdot}CO$, 27·1%). The diacetyl derivative of the compound suggested by Decker and Fellenberg would have the formula $C_{26}H_{26}O_5$ and would require C, 74·6; H, 6·2; $CH_3{\cdot}CO$, 28·2%.

The Carbomethoxy-derivative of Compound A was prepared by the recognised method and formed colourless needles, m. p. 184° with shrinking at 179°; it was soluble in organic solvents but insoluble in cold alkali, which, however, caused hydrolysis on warming (Found: C, 71·0, 71·3; H, 6·0, 6·0%). The dicarbomethoxy-derivative of the compound $C_{22}H_{22}O_3$ would have the formula $C_{26}H_{26}O_7$ and would require C, 69·3; H, 5·8%.

2-Hydroxystyryl n-*Propyl Ketone.*—A solution of salicylaldehyde (50 g.) and methyl *n*-propyl ketone (50 g.) in alcohol (100 c.c.) was gradually added to aqueous sodium hydroxide (500 c.c. of 10%). The mixture when warmed on a water-bath for 10 minutes turned red, and after 24 hours deposited long, yellow needles of the sodium salt of the ketone. These were acidified in aqueous solution, and the faintly coloured precipitate of the free ketone produced crystallised from benzene in colourless needles, m. p. 113° (Found: C, 75·7; H, 7·3. $C_{12}H_{14}O_2$ requires C, 75·8; H,

7·4%). The filtrate obtained after removal of the yellow sodium salt, on saturation with carbon dioxide, gave a yellow precipitate, which crystallised from cold aqueous alcohol in yellow plates, m. p. 113° (Found: C, 75·7; H, 7·3. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%).

2-*Hydroxystyryl* n-*Hexyl Ketone*.—Salicylaldehyde (5 g.) and methyl *n*-hexyl ketone (5 g.) were treated with a mixture of alcohol (100 c.c.) and aqueous sodium hydroxide (30 c.c. of 30%). After 7 days, a light orange colour developed in the solution which, on neutralisation with carbon dioxide, furnished a yellow precipitate. Careful crystallisation from cold aqueous alcohol resulted in the formation of yellow plates, m. p. 102—103°, which were very unstable and passed on standing into a colourless isomeride of identical melting point (Found: C, 77·2; H, 8·7. $C_{15}H_{20}O_2$ requires C, 77·6; H, 8·6%).

3-*Methoxy*-4-*hydroxystyryl Ethyl Ketone*.—A mixture of vanillin (50 g.), methyl ethyl ketone (78 g.), and aqueous sodium hydroxide (150 c.c. of 10%) was warmed on a water-bath for 5 minutes, a red colour soon appearing. After 3 days, the solution was poured into 3 litres of water, filtered, and the filtrate saturated with carbon dioxide. The yellow solid obtained crystallised from benzene–hexane in yellow needles, m. p. 93°, which were readily soluble in alcohol, benzene, acetone, or chloroform, and sparingly soluble in water or hexane. The *ketone* dissolved in alkali to form a yellow solution, which assumed a red tint after 3 weeks' exposure (Found: C, 69·5; H, 6·9. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%). The colourless isomeride is readily obtained from the yellow form in the usual way and when crystallised from aqueous solvents it separates as a yellow hydrate, m. p. 79—82° (Found: C, 63·9; H, 7·2. $C_{12}H_{14}O_3,H_2O$ requires C, 64·3; H, 7·1%). On dehydration the hydrate lost water (8·62%, theory requiring 8·73%), yielding colourless needles (m. p. 93°), which were also formed by crystallising the yellow form from non-aqueous solvents in presence of a trace of acid (Found: C, 69·6; H, 6·8%).

3-*Methoxy*-4-*hydroxystyryl* n-*Propyl Ketone*.—Vanillin (50 g.) and methyl *n*-propyl ketone (28 g.) were dissolved in alcohol (150 c.c.), and aqueous sodium hydroxide (300 c.c. of 20%) was added. The mixture was warmed for a few minutes on a water-bath, when a red colour developed. On allowing to stand for 3 days and then pouring into excess of dilute sulphuric acid, a yellow oil separated which solidified on leaving in the ice-chest. It crystallised from aqueous acetone in yellow cubes, m. p. 83°, which were soluble in alcohol, benzene, or acetone (Found: C, 70·5; H, 7·3. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%). The filtrate from the yellow oil, on

standing for 2 days in the ice-chest, deposited colourless needles, m. p. 83°, which could also be produced from the yellow compound by the ordinary methods of isomerisation (Found : C, 70·6; H, 7·3%). The yellow alkaline solutions of both isomerides turned red on prolonged standing.

3 : 4-Methylenedioxystyryl methyl ketone.			3-Methoxy-4-hydroxystyryl methyl ketone.		
	Solubility in g. per 100 g. of alcohol of			Solubility in g. per 100 g. of alcohol of	
Temp.	Yellow isomeride.	Colourless isomeride.	Temp.	Yellow isomeride.	Colourless isomeride.
20°	1·5	1·2	18°	4·4	4·8
22	1·8	1·5	30	9·0	10·1
31	4·0	2·6	38	12·1	13·7
36	5·5	3·3	39	12·4	—
43	8·0	—	47	16·0	18·6
50	—	4·9			

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CCCLI.—*The Relationship of Salts in Dilute Aqueous Solution as determined by their Influence on the Critical Solution Temperature of the System Phenol–Water.*

By JOHN HERBERT CARRINGTON, LOUIS ROBERT HICKSON, and WILLIAM HAMILTON PATTERSON.

THE investigation (Duckett and Patterson, *J. Physical Chem.*, 1925, **29**, 295) of the rise of the critical solution temperature (C.S.T.) of the system phenol–water due to the addition of a salt soluble only in the aqueous phase has been continued.

The C.S.T. of phenol–water (temperature for standard turbidity) was taken as 66·0°. The point of standard turbidity was more reproducible than that of appearance or disappearance of faint opalescence, which occurred about 2·5° higher. The standard was determined in all the experiments by the first appearance or disappearance of the thermometer bulb when viewed through the liquid with constant illumination. The system itself, and the bath in which it was placed, were stirred vigorously throughout. The temperatures determined were easily reproducible within 0·05°.

Owing to the flatness of the miscibility curve in the region of

the C.S.T., no change of the latter could be observed when the percentage of phenol was varied between the limits 34·2 and 37·8; consequently salt hydrates could be added without causing error. All mixtures were, however, made to contain 36·0—36·1% of phenol, and known weights of pure salts were added. Deliquescent salts and acids were added in the form of standard solutions. Jena glass was used in the case of fluorides.

The results are stated in the tables in terms of C = number of g.-mols. of solute per 1000 g. of total mixture; e = elevation of C.S.T.; and $E = e/C$ = molecular elevation of C.S.T.

In the normal case of solubility of the salt in the aqueous phase only, absence of hydrolysis, and of complex formation, e is nearly proportional to C at higher concentrations; the deviation from linear relationship for zero concentration upwards becomes clearer on plotting E against C. This deviation is accentuated in abnormal cases.

The values of e and E given in the tables are obtained for fixed concentrations by interpolation from curves. A bracketed number indicates slight extrapolation. Values are given for hydrochloric and sulphuric acids, and in a few cases values are reproduced, with slight corrections at the higher concentrations (since precautions were taken in these experiments to prevent evaporation), from the earlier paper. Abnormal cases due to hydrolysis, complex formation, and chemical action are not included in the tables, since this paper deals primarily with normal behaviour. Nevertheless a few remarks on these abnormal cases may be made in passing.

Hydrolysis.—Lithium carbonate in common with the other alkali carbonates produces a lowering of the critical solution temperature. Sodium acetate produces a slight lowering, and sodium cyanide a much greater one. The method is very sensitive for detecting hydrolysis under the experimental conditions, *viz.*, at 60—70° and in the presence of phenol. In such a case, the numerical value of E decreases with increasing concentration, *e.g.*, for sodium acetate, $C = 0{\cdot}013$, $E = -14{\cdot}5$; $C = 0{\cdot}318$, $E = -1{\cdot}4$.

Hydrolysis may be thus distinguished from cases where a lowering is due to solubility in the ordinary way in both phases, *e.g.*, with sucrose or urea. In this case, E remains practically constant (Duckett and Patterson, *loc. cit.*).

Complexity.—Even in the case of single salts complexes are sometimes formed in solution. This is especially so for cadmium iodide, less so for the bromide, and still less for the chloride. Cadmium sulphate behaves normally up to $C = 0{\cdot}045$, and the nitrate up to a higher concentration.

TABLE I.

Values of e.

Salt.	Molecular concentrations. 0·01.	0·02.	0·03.	0·04.	0·05.	0·10.	0·15.	0·20.	0·30.
NH_4F	(0·35°)	0·68°	1·0°	1·25°	1·55°	2·75°	3·95°	4·95°	7·0°
HCOONa	(0·50)	1·00	1·45	1·9	2·3	4·35	6·3	8·15	11·7
NH_4NO_3	—	—	—	(2·1)	2·4	4·3	5·95	7·5	10·2
NaF	(0·60)	1·15	1·75	2·2	2·7	5·2	7·5	9·6	13·6
$KClO_3$	(0·70)	(1·30)	1·85	2·4	2·95	5·35	7·5	9·5	—
KNO_3	(0·80)	1·55	2·15	2·75	3·3	5·9	8·3	10·4	(14·85)
KI	(0·70)	1·55	2·15	2·75	3·3	5·9	8·2	10·4	14·9
NH_4Br	—	1·5	2·2	2·8	3·45	6·2	8·7	11·2	15·6
$KBrO_3$	(0·80)	1·5	2·2	2·9	3·5	6·3	8·7	10·8	—
LiI	(0·80)	1·5	2·2	2·9	3·5	6·3	8·75	11·0	(15·4)
HCl	(0·85)	1·6	2·4	3·1	3·75	6·7	9·3	11·75	15·8
NH_4Cl	—	(1·7)	2·5	3·15	3·9	7·2	9·8	12·5	17·6
$NaNO_3$	(0·80)	1·55	2·3	3·0	3·75	7·1	10·1	12·9	—
NaI	(0·90)	1·6	2·3	3·0	3·7	6·8	9·6	12·3	—
KBr	(1·0)	(2·0)	2·9	3·7	4·45	7·9	11·2	14·3	(20·5)
KCl	(1·1)	2·0	3·0	3·95	4·7	8·7	12·3	16·0	—
NaBr	(1·2)	2·35	3·35	4·3	5·2	9·2	12·95	16·5	—
LiCl	(1·2)	(2·4)	3·4	4·4	5·3	9·6	13·8	17·6	(25·1)
NaCl	(1·3)	(2·5)	(3·55)	(4·5)	5·45	10·0	14·5	18·95	—
H_2SO_4	1·55	2·95	4·2	5·3	6·35	11·3	—	—	—
$Pb(NO_3)_2$	1·55	3·05	4·3	5·55	6·75	12·2	17·7	(23·4)	—
NaH Tartrate	—	(3·5)	4·9	6·2	7·4	13·2	(19·2)	—	—
$Cd(NO_3)_2$	2·0	3·65	5·1	6·55	8·0	(14·2)	—	—	—
$CdCl_2$	2·45	3·4	6·1	7·55	9·0	(15·7)	—	—	—
$CuCl_2$	2·5	4·8	6·65	8·3	9·9	(16·7)	—	—	—
$(NH_4)_2SO_4$	2·5	4·75	6·65	8·5	10·05	17·9	—	—	—
$CoCl_2$	2·85	5·15	7·25	9·25	11·25	(20·7)	—	—	—
$CaCl_2$	2·85	5·15	7·25	9·25	11·25	(20·7)	—	—	—
$BaCl_2$	2·85	5·15	7·25	9·25	11·2	21·6	—	—	—
$SrCl_2$	2·85	5·15	7·25	9·25	11·2	(21·6)	—	—	—
$MgCl_2$	2·9	5·25	7·4	9·5	11·4	—	—	—	—
K_2SO_4	3·2	5·5	7·8	10·0	12·2	—	—	—	—
$BeSO_4$	3·2	5·8	8·2	10·4	12·6	—	—	—	—
$CuSO_4$	3·2	6·0	8·7	11·2	13·6	—	—	—	—
Li_2SO_4	3·7	6·7	9·25	11·7	14·1	—	—	—	—
Na_2SO_4	3·9	7·1	9·7	12·4	15·1	—	—	—	—
$ZnSO_4$	3·7	6·8	9·7	12·5	15·3	—	—	—	—
$CoSO_4$	3·7	6·8	9·85	12·7	15·7	—	—	—	—
$CdSO_4$	3·7	6·8	9·9	12·7	15·8	—	—	—	—
$MgSO_4$	4·05	7·3	10·2	13·2	16·2	—	—	—	—
$NiSO_4$	4·1	7·45	10·6	13·8	17·1	—	—	—	—

Molecular concentrations.	0·005.	0·01.	0·02.	0·03.	0·04.	0·05.
Sodium Citrate	2·95°	5·1°	8·9°	12·65°	15·9°	19·4°
$Cr_2(SO_4)_3$	3·5	5·5	10·0	(14·6)	—	—
$Al_2(SO_4)_3$	3·9	7·1	13·2	—	—	—
$Na_4Fe(CN)_6$	4·4	7·7	(14·2)	—	—	—

The formation of complex molecules and ions under varied conditions in different solutions will be dealt with in a subsequent communication.

Chemical Action.—In some cases chemical action is evident,

Table II.

Values of E.

Salt.	Molecular concentrations. 0·01.	0·02.	0·03.	0·04.	0·05.	0·10.	0·15.	0·20.	0·30.
NH_4F	—	34°	33°	31·2°	31·1°	27·5°	26°	25°	23·5°
$HCOONa$	—	49	47·7	46·4	45·6	43·4	41·9	40·8	39
NH_4NO_3	—	—	—	—	(47·4)	42·1	39·7	37·6	33·5
NaF	—	—	58·0	55·2	54·0	51·2	49·4	47·9	45·2
$KClO_3$	—	(66·4)	63·0	61·2	59·6	54·3	50·8	47·6	—
KNO_3	—	77·2	72·0	68·4	65·9	59·6	55·6	52·8	(50)
KI	—	—	71·2	68·6	66·6	59·7	55·0	52·2	49·9
NH_4Br	—	75·0	72·7	70·4	68·6	62·1	57·9	55·1	51·9
$KBrO_3$	—	75·0	73·0	72·5	70·0	63·0	58·0	54·0	—
LiI	—	78·0	74·8	72·0	69·6	61·8	57·4	54·3	(50·6)
HCl	—	—	80·5	78·0	75·5	67·1	61·7	57·7	53·8
NH_4Cl	—	—	(79·4)	77·2	75·6	69·6	65·6	62·8	(58·6)
$NaNO_3$	—	79·7	77·8	76·4	75·2	70·8	67·3	64·8	—
NaI	—	81·0	78·1	76·0	74·3	68·2	64·3	61·6	—
KBr	—	—	97·2	92·0	89·2	79·8	74·5	71·6	—
KCl	—	106	101·	97·6	95·1	86·5	81·7	78·4	—
$NaBr$	—	(116)	111	106	103	93·1	86·8	82·7	—
$LiCl$	—	(124)	116	110	107	97·6	92·4	88·7	(83)
$NaCl$	—	—	—	—	110	100	96·4	93·7	—
H_2SO_4	157	146	139	134	130	113	—	—	—
$Pb(NO_3)_2$	161	149	142	137	134	121	117	(117)	—
NaH Tartrate	—	—	160	153	147	133	(127)	—	—
$Cd(NO_3)_2$	197	181	173	166	161	—	—	—	—
$CdCl_2$	247	212	198	188	180	157	—	—	—
$CuCl_2$	270	242	221	205	199	171	—	—	—
$(NH_4)_2SO_4$	252	230	218	209	202	176	—	—	—
$CoCl_2$	—	255	241	231	223	200	—	—	—
$CaCl_2$	—	255	241	228	221	201	—	—	—
$BaCl_2$	—	255	241	228	221	204	—	—	—
$SrCl_2$	—	255	241	231	223	206	—	—	—
$MgCl_2$	296	262	247	237	230	207	—	—	—
K_2SO_4	326	282	269	257	248	226	—	—	—
$BeSO_4$	318	290	273	262	254	—	—	—	—
$CuSO_4$	—	304	288	278	274	(269)	—	—	—
Li_2SO_4	367	332	307	294	283	(257)	—	—	—
Na_2SO_4	388	350	321	308	300	—	—	—	—
$ZnSO_4$	371	339	321	311	305	—	—	—	—
$CoSO_4$	375	348	334	323	315	—	—	—	—
$CdSO_4$	375	348	334	323	320	—	—	—	—
$MgSO_4$	390	357	341	329	323	—	—	—	—
$NiSO_4$	410	373	354	344	340	—	—	—	—

Molecular concentrations.	0·005.	0·01.	0·02.	0·03.	0·04.	0·05.
Sodium Citrate	568°	510°	455°	416°	396°	388°
$Cr_2(SO_4)_3$	700	550	500	487	—	—
$Al_2(SO_4)_3$	770	720	(660)	—	—	—
$Na_4Fe(CN)_6$	872	772	—	—	—	—

e.g., with complex cobalt salts. In the case of sulphuric acid, the result is abnormally low, as will be seen by comparing its values relative to those of sodium sulphate with the values of hydrochloric acid relative to those of sodium chloride. It is possible

that reaction with the phenol may have taken place to some extent even at the concentrations employed. (The possibility of the first stage of ionisation having taken place may also account for the low result.) In other cases, *e.g.*, copper sulphate, the action is only very slight. Such salts are therefore included.

Discussion.

Returning to cases of apparently normal solution as given in the tables, no precise explanation can yet be offered of the numbers associated with different salts nor of their variation with concentration. Previous results and those which follow become explicable when interpreted on an hypothesis of hydration. Some light may be thrown on the question of the part played by the ions or the undissociated salt by experiments to be undertaken with the isomeric chromic chloride hexahydrates, which are supposed to give rise to different numbers of ions. At the present stage the following conclusions may be drawn :

(1) Anions and kations may be arranged qualitatively in order of diminishing effect on C.S.T.

Citrate, sulphate, hydrogen tartrate, chloride, bromide, bromate, nitrate = iodide, chlorate, formate.

Ni, Mg, Cd, Co = Ba = Sr = Ca, Zn, Cu, Be, Pb, Na, Li, K, NH_4, H.

(2) The effect of the anion is in general greater than that of the kation.

(3) Definite values cannot be attributed to the ions, since the value is modified according to the identity of the other ion in the compound; *e.g.*, values of E : Na—K, 8·5 from NaI—KI, 15 from NaCl—KCl, and 26 from $\frac{1}{2}Na_2SO_4$—$\frac{1}{2}K_2SO_4$.

(4) The effect in general decreases with increasing atomic weight of the elements in the various groups of the periodic system, the first member, however, being always out of place :

Na, *Li*, K; Mg, Ca = Sr = Ba, *Be*; Cl, Br, I, *F*.

(5) If log e is plotted against log C, a series of parallel straight lines is obtained, *i.e.*, $\log e = b \log C + x$ or $e = aC^b$, where b is a constant characteristic of the phenol–water system (actually its value varies between 0·83 and 0·87), and a is a specific constant for each salt.* The similarity of this equation to that of the Freundlich adsorption isotherm may be regarded as supporting the suggestion of Hildebrand (" Solubility ") that the solution of one liquid in another is an extreme case of adsorption. It has already been shown (*loc. cit.*) that if the anions are placed in the order of their effectiveness in raising the C.S.T., the series is almost identical

* For *salts* which lower the C.S.T., *i.e.*, are soluble in both phases, the same equation applies, with a different value for b.

with the Hofmeister series for the coagulation of neutral egg-albumin. This further supports the view that the former phenomenon may be associated with adsorption.

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CCCLII.—*Studies of Equilibrium in Systems of the Type* $Al_2(SO_4)_3$–M″SO_4–H_2O. *Part II. Aluminium Sulphate–Nickel Sulphate–Water at* 30°.

By ROBERT MARTIN CAVEN and THOMAS CORLETT MITCHELL.

As events have arisen which will prevent the continuance of this work by one of the authors, it has been decided to publish the results obtained to date. The present contribution is a continuation of work already reported (this vol., p. 527).

The equilibrium mixtures were obtained in a manner similar to that used in the preparation of those for the manganese system.

Weighed amounts of the solutions and moist solid phases were then made into solutions measuring known volumes, from which aliquot portions were removed for analysis.

Nickel was estimated with potassium cyanide, with silver iodide as indicator (Moore's method), and aluminium was calculated after determination of the total sulphate.

During the estimation of nickel, aluminium was kept in solution by dissolving in ammonia the precipitate formed by addition of sodium pyrophosphate to the mixture (*vide* Sutton's "Volumetric Analysis," 1924, p. 278).

At first some difficulty was experienced, the tendency for false end-points to occur (see Sutton) followed by development of opalescence on standing being decidedly troublesome. The following procedure, however, proved extremely satisfactory and enabled trustworthy results to be obtained quickly and with regularity.

To an aliquot portion of the mixed solution sodium pyrophosphate was added until the precipitate first formed began to redissolve. The precipitate was then completely dissolved by the addition of excess of ammonia; the resultant solution was diluted to working volume, and the ammonia almost neutralised with dilute sulphuric acid, leaving the solution faintly ammoniacal. The titration was then carried out in the usual way.

The quantities in the table are expressed as g. per 100 g. of solution (for the solutions) or of moist solid (for the rests).

Solutions.			Rests.			
$Al_2(SO_4)_3$.	$NiSO_4$.	H_2O.	$Al_2(SO_4)_3$.	$NiSO_4$.	H_2O.	Solid phase.
28·86	Nil	71·14	—	—	—	Aluminium sulphate.
25·87	4·74	69·39	48·71	0·82	50·47	„ „
21·95	10·87	67·18	49·81	0·51	49·68	„ „
21·30	12·91	65·79	29·99	9·91	60·10	„ „ *
20·79	13·29	65·92	4·03	55·40	40·57	Nickel sulphate.
15·29	17·53	67·18	3·01	52·17	44·82	„ „
8·70	22·56	68·74	0·35	55·89	43·76	„ „
7·34	23·58	69·08	1·13	52·70	46·17	„ „
5·29	26·03	68·68	0·45	57·65	41·90	„ „
Nil	30·77	69·23	—	—	—	„ „

* This solid phase was separated very near to the triple point and appears to contain some nickel as well as aluminium sulphate.

Conclusion.—There is no evidence of double salt formation between aluminium sulphate and nickel sulphate in solution at 30°.

The authors desire to express their thanks to the Governors of the Royal Technical College for assistance that has enabled one of them (T. C. M.) to participate in this research.

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CCCLIII.—*The System Silver Sulphate–Aluminium Sulphate–Water at* 30°.

By Robert Martin Caven and Thomas Corlett Mitchell.

The present communication deals with an attempt to settle the question of the existence of silver alum.

Previous investigators are not in agreement; for whilst Kern (*Chem. News*, 1875, **31**, 209) claims to have made typical crystals of silver alum, $Ag_2SO_4,Al_2(SO_4)_3,24H_2O$, by evaporation of a mixed solution of the component salts, and Church and Northcote (*ibid.*, 1864, **9**, 155) describe its preparation by heating a mixture of silver sulphate, aluminium sulphate, and water in a sealed tube until all the silver salt dissolved, Wilkie, in this laboratory, has repeated both methods without success.

Two methods were employed in making up the equilibrium mixtures. In the first, recrystallised silver sulphate was stirred continuously for several days with a solution of aluminium sulphate in a thermostat at $30° \pm 0·1°$.

The second method consisted in evaporating isothermally, with the aid of a current of filtered air, a mixed solution of the constituents. The mixture was stirred while evaporation was going

on, and for 2 days after a sufficient quantity of solid phase had accumulated.

The solution and solid phases were separated in the usual way, weighed, made up to known volumes, and aliquot portions taken for analysis.

Silver could not be estimated by simple precipitation of the chloride, as it was found that silver chloride dissolved in aluminium chloride solution on heating—indeed, if hydrochloric acid was used to precipitate the silver, considerable quantities of silver chloride could be dissolved. It is hoped later to investigate this phenomenon; meantime attention is directed to the great tendency to form double salts in the anhydrous state exhibited by aluminium chloride and described by Baud (*Compt. rend.*, 1901, **133**, 869; *Ann. Chim. Phys.*, 1904, **1**, 8) and Kendall, Crittenden, and Miller (*J. Amer. Chem. Soc.*, 1923, **45**, 963).

Silver was estimated by electrolysis of the double cyanide solution as recommended in text-books on electro-analysis. The aluminium was subsequently estimated by precipitation as hydroxide after the destruction of the cyanide by heating with sulphuric acid.

Mols. Ag_2SO_4 per 1000 g. H_2O.	Mols. $Al_2(SO_4)_3$ per 1000 g. H_2O.	Solid phase.
0·0285	Nil	Ag_2SO_4
0·0292	0·0777	,,
0·0304	0·1449	,,
0·0306	0·3026	,,
0·0306	0·5114	,,
0·0308	0·8153	,,
0·0310	0·9210	,,
0·0314	1·276	$Ag_2SO_4 + Al_2(SO_4)_3,18H_2O$
Nil	1·187	$Al_2(SO_4)_3,18H_2O$

The continuous increase in the solubility of silver sulphate was most marked, but seems in no way extraordinary in view of the results for the systems silver sulphate–potassium sulphate, silver sulphate–ammonium sulphate, and silver sulphate–sodium sulphate recorded by Barre (*Ann. Chim.*, 1911, **24**, 149, 202, 210; *Compt. rend.*, 1910, **150**, 1323). Ephraim and Wagner (*Ber.*, 1917, **50**, 1103) found as the result of a single determination, that silver sulphate was more soluble in aluminium sulphate solution than in water.

Conclusion.—From the results obtained it is evident that silver sulphate and aluminium sulphate do not form a crystalline alum from mixtures of their solutions at 30°.

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CCCLIV.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXVII. The Optical Properties of* n-*Alkyl* p-*Toluenesulphinates.*

By Henry Phillips.

Optically active *n*-alkyl *p*-toluenesulphinates can be prepared by methods described in this communication. This discovery is difficult to reconcile with the formula $RO{\cdot}S(:O){\cdot}C_7H_7$, by which the constitution of these esters is indicated by the classical theories of valency. It will be suggested that the formula $RO{\cdot}\overset{+}{S}(\cdot\overset{-}{O}){\cdot}C_7H_7$, assigned to these esters by the later electronic theories of valency is more in agreement with the new results. It will then be deduced, from a consideration of the known constitutions of other optically active compounds, that the newly discovered asymmetric complex is associated with an atom, in this instance a sulphur atom, bearing a positive charge and in combination with three different groups or atoms. It will be pointed out that this deduction has a bearing on the phenomenon of complex rotatory dispersion exhibited by the esters of carboxylic acids derived from optically active secondary alcohols.

The asymmetric sulphinic ester molecule has also been shown to possess a certain mobility, since *p*-toluenesulphinic esters of *l*-β-octanol and of *l*-menthol which contain the *p*-toluenesulphinoxy-radical in an optically active state exhibit marked mutarotation.

Evidence is also given that, when an ester of *p*-toluenesulphinic acid undergoes alkyloxy-interchange, $\dot{\overset{-}{O}}{\cdot}\overset{+}{S}\!<\!\begin{matrix}OR'\\C_7H_7\end{matrix} \longrightarrow \overset{-}{O}{\cdot}\overset{+}{S}\!<\!\begin{matrix}OR''\\C_7H_7\end{matrix}$, the optically active ester produced has the opposite configuration to that of the original ester. The system, newly discovered to be asymmetric, thus appears capable of undergoing a reaction which is an analogue of the Walden inversion in optically active carbon compounds.

The asymmetric character of the *p*-toluenesulphinic ester molecule is destroyed on oxidation, and the chemical character of the *p*-toluenesulphonic ester produced differs considerably from that of the parent ester. This difference is illustrated by a description of certain reactions of the *p*-toluenesulphonic esters of *l*-β-octanol and of *l*-menthol which lead to the formation of esters of *d*-β-octanol and of *d*-*neo*menthol, respectively.

Preparation and General Properties of p-*Toluenesulphinic Esters.*

The literature dealing with the preparation of esters of the aromatic sulphinic acids is confined to a few papers by Otto and Rossing (*Ber.*, 1885, **18**, 2439; 1886, **19**, 1224); these authors prepared their esters by the interaction of the sodium salts of the acids with the chlorocarbonates of the alcohols. Owing to impurities arising through the occurrence of side reactions, the esters could not be distilled and possibly methyl β-naphthalenesulphinate (*Ber.*, 1892, **25**, 230), which is a solid, is the only pure ester of a sulphinic acid which has hitherto been described.

The *p*-toluenesulphinic esters used in this investigation were prepared by the direct action of *p*-toluenesulphinyl chloride on the alcohols, potassium carbonate or pyridine being used to remove the hydrogen chloride eliminated. *l*-Menthyl and *l*-β-octyl *p*-toluenesulphinates were also prepared by the displacement of the ethoxy-group of ethyl *p*-toluenesulphinate by warming that ester with the alcohols under reduced pressure. The *p*-toluenesulphinates of the lower aliphatic alcohols and of *l*-β-octanol were obtained as colourless liquids which did not crystallise when cooled by liquid air. The crude esters can be distilled at very low pressures, but show some tendency to decompose. On redistillation, this tendency is less marked, but is regained when the redistilled ester is kept in a closed glass vessel for several days. When exposed to moist air, they are oxidised slowly and are partly hydrolysed, depositing crystals of *p*-toluenesulphinic acid. They can, however, be readily oxidised to the corresponding sulphonates by potassium permanganate.

The Preparation of the n-*Alkyl Esters of* p-*Toluenesulphinic Acid in an Optically Active State.*

The method adopted was to heat gently a mixture of two molecular proportions of the optically inactive *n*-alkyl ester with one of *l*-β-octanol, under reduced pressure; the mixture of a lævorotatory *n*-alkyl *p*-toluenesulphinate and a lævorotatory β-octyl *p*-toluenesulphinate produced could be separated by systematic fractional distillation at very low pressures. In this manner, using optically inactive ethyl *p*-toluenesulphinate with $n_D^{25^\circ}$ 1·5309, lævorotatory ethyl *p*-toluenesulphinate was separated with $n_D^{25^\circ}$ 1·5309 and $\alpha_{5461}^{25^\circ}$ −6·72°.* As is to be expected, alcoholysis † of

* In the theoretical part of this paper, all observed rotations are quoted for comparative purposes as if obtained in a tube of 1 dcm.

† Treatment with a solution of potassium acetate in an excess of anhydrous ethyl alcohol. The potassium acetate was added in order to contrast its behaviour towards ethyl-alcoholic solutions of *p*-toluene-sulphinic and -sulphonic esters.

the lævorotatory β-octyl *p*-toluenesulphinate simultaneously produced gave dextrotatory ethyl *p*-toluenesulphinate, with $n_D^{25°}$ 1·5309 and $\alpha_{5461}^{25°}$ + 0·92°.

It was not found possible by mixing (*a*) *l*-β-octanol or (*b*) lævorotatory β-octyl *p*-toluenesulphinate with inactive ethyl *p*-toluenesulphinate to prepare solutions which would imitate in refractive index as well as in rotatory power the lævorotatory ethyl ester described above. Further, this ester on oxidation gave a quantitative yield of the optically inactive ethyl *p*-toluenesulphonate.

By a similar method to that outlined above, using optically inactive *n*-butyl *p*-toluenesulphinate with $n_D^{25°}$ 1·5195, a lævorotatory *n*-butyl *p*-toluenesulphinate was isolated with $n_D^{25°}$ 1·5195 and $\alpha_{5461}^{25°}$ − 3·46°, and by the alcoholysis of a highly lævorotatory menthyl *p*-toluenesulphinate a dextrorotatory ethyl *p*-toluenesulphinate was obtained with $n_D^{25°}$ 1·5309 and $\alpha_{5461}^{25°}$ + 16·52°.

Since the *n*-alkyl *p*-toluenesulphinates have thus been obtained in optically active forms, *p*-toluenesulphinyl chloride also may exist in enantiomorphous modifications.

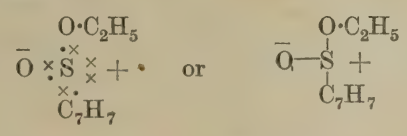
Some evidence of this was obtained by treating two molecular proportions of *p*-toluenesulphinyl chloride with one molecular proportion of either *l*-β-octanol or of *l*-menthol in solution in pyridine, when the resulting mixture apparently contained the excess *p*-toluenesulphinyl chloride in an optically active condition; for when such mixtures were treated with aniline, *p*-toluenesulphinanilide was obtained with a small lævorotatory power. Further, after treatment of similar mixtures with a solution of ethyl alcohol in pyridine, although in two experiments the ethyl *p*-toluenesulphinate finally isolated was optically inactive, in a third experiment an impure ethyl ester was obtained which was dextrorotatory.

The Conditions underlying the Asymmetry of an Atom in Combination with Three Different Groups or Atoms.

The discovery that the *n*-alkyl *p*-toluenesulphinates can be obtained in an optically active state throws a new light on the factors which are associated with the occurrence of asymmetry in a molecule made up of an atom in combination with three different groups or atoms. Before these factors can be determined it is necessary to indicate briefly those concepts of the electronic theory of valency, as developed by Sir J. J. Thomson, Lewis, Kossel, Langmuir, and others, which are now adopted to derive a constitutional formula for sulphinic esters more amenable to treatment from the point of view of the classical theories of stereochemistry than the usually accepted formula, $RO{\cdot}S(:O){\cdot}C_7H_7$. They are (*a*) that the chemical properties of the elements of the first two

short periods of the Periodic Table can be explained by their tendency to give up or to share electrons until the arrangement and number of electrons in their valency shells attain those existing in the inert gases, (*b*) that the manner of their sharing or taking up of electrons is defined by the terms covalency and electrovalency. An additional proviso (compare Lowry, *Trans. Faraday Soc.*, 1923, **18**, 285) is made, that, should one atom contribute both electrons to the formation of a duplet by which its union with another atom is typified, such an arrangement would give rise to a so-called " semipolar " double bond, or, in other words, a covalency and an electrovalency. The centres of combined atoms will, however, still be considered to occupy those positions to which they have so far been allotted by the classical stereochemical theories, *e.g.*, the centres of the atoms united by four covalencies to a carbon atom are at the corners of a tetrahedron which circumscribes that atom, but the position of the electrons which form the covalencies need not be necessarily situated or fixed on the lines joining the centre of the carbon atom to the centres of the other four atoms.

In the " electronic " formula for ethyl *p*-toluenesulphinate given below, it is desired to direct particular attention to the valency electrons of the sulphur atom and they are therefore represented as crosses. Electrons in the completed outer shell of this atom which are contributed by the atoms with which it is united are signified by the conventional dot, as is also that particular sulphur electron which virtually acts as an oxygen electron on the formation of the " semipolar " double bond.



Experimental evidence was lacking for the postulated existence of a covalency and an electrovalency between the sulphur and sulphoxyl oxygen atoms, but has been obtained in the following manner.

Sugden (J., 1924, **125**, 1177), using the relation between surface tension and density discovered by Macleod (*Trans. Faraday Soc.*, 1923, **10**, 36), makes a comparison of the molecular volumes of liquids at temperatures at which they have the same surface tension; such molecular volumes, or parachors, P, being defined by the equation $P = M/D \cdot \gamma^{1/4}$, in which the symbols have their usual significance.

The parachors of elements can be deduced from molecular parachors, on which the effect of unsaturation is great; thus the double bond between carbon and carbon, oxygen and carbon, or

nitrogen and oxygen has the value 23·2. More recently, Sugden, Reed, and Wilkins (this vol., p. 1525) have shown that, in a series of compounds the accepted formulæ of which contain double bonds which on the formulation of Lowry (*loc. cit.*) would be more accurately represented by a covalency and an electrovalency, the parachor of such linkings is −1·6. *P* for a " semipolar " double bond is therefore −1·6.

Dr. Sugden kindly undertook the determination of the parachor of ethyl *p*-toluenesulphinate with $n_D^{25°}$ 1·5309, $d_4^{25°}$ 1·114. His determinations are recorded in Table III (p. 2570). The observed parachor, 410·3, agrees very closely with the parachor of 410·7 calculated on the assumption that the bond between the sulphur and sulphoxyl oxygen atom is " semipolar "; if it were a non-polar double bond the calculated parachor would be 435·5.

Having thus rendered very probable the existence of a " semipolar " bond in the formula of the ester given above, an attempt can now be made to pick out the essential conditions underlying the asymmetry of the sulphur atom it contains. This can best be done by setting out these supposed essential conditions and adding to or subtracting from their number those conditions which a study of other known asymmetric systems indicates are wanting or unnecessary.

As a preliminary hypothesis, the following could be adopted—that the sulphur atom is asymmetric since it has three different groups attached to it, and possesses a " lone pair " of electrons which renders the system analogous to that by which an asymmetric carbon atom is surrounded. If this be true, then the optical activity shown by the *d*-methylethylthetine *d*-camphorsulphonate (I) of Pope and Peachey (J., 1900, **77**, 1072) may be partly due to the same cause.

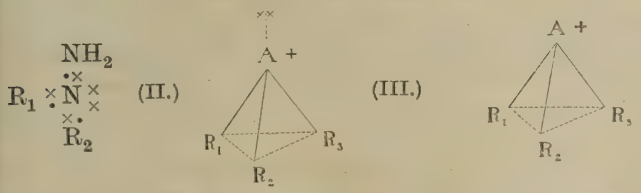
$$\left[\begin{array}{l} \quad CH_2{\cdot}CO_2H \\ C_2H_5 \times\overset{\bullet\times}{\underset{\times\bullet}{S}}\times + \\ \quad CH_3 \end{array}\right] \bar{O}{\cdot}SO_2{\cdot}C_{10}H_{15}O \qquad (I.)$$

The structural resemblance between the positive ion of this salt and ethyl *p*-toluenesulphinate is striking. The above formulation also explains why the *d*-camphorsulphonoxy-ion can be readily replaced by others without the racemisation which so often accompanies the replacement of groups attached to an asymmetric carbon atom. This activity of the positive methylethylthetine ion not only agrees with the preliminary hypothesis, it also sanctions the dismissal of a further possible condition of asymmetry—namely—that one of the three groups attached to the central atom should carry a negative charge. This simplification is necessary in order that the

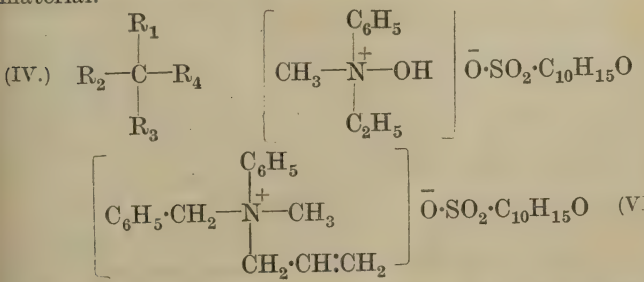
lack of asymmetry of tervalent nitrogen can be considered. Tervalent nitrogen, indeed, satisfies all the conditions laid down in the preliminary hypothesis, and yet all attempts to resolve substituted ammonias or unsymmetrical hydrazines (II) have been unsuccessful (Reychler, *Bull. Soc. chim.*, 1902, **27**, 979; Jones and Millington, *Proc. Camb. Phil. Soc.*, 1904, **12**, 489).

The failure, in spite of numerous attempts during the last thirty years, to accomplish the resolution of a compound the asymmetry of which could be associated with a tervalent nitrogen atom, has led Meisenheimer (*Ber.*, 1923, **56**, 1353) to the conclusion that such an atom cannot give rise to an asymmetric molecule.

To bring the preliminary hypothesis into line with Meisenheimer's conclusion, it can be amended as follows—a sulphur atom, or any other atom, is asymmetric when it is attached to three dissimilar groups, is in possession of a lone pair of electrons, and carries a positive charge (or alternatively has lost an electron). If such a system be represented graphically in three-dimensional space on the lines of the classical theory of van 't Hoff (III), it becomes apparent that the amended hypothesis may contain one unnecessary condition, namely, the possession by the atom of a lone pair of electrons.



For if it remained a necessary condition, a consideration of demonstrated asymmetry associated with quadrivalent systems indicates that the presence or absence of a positive charge is immaterial.



The asymmetry of the carbon atom in (IV) and of the methylethylaniline oxonium ion (V), shown to exist in optically active forms by Meisenheimer (*Ber.*, 1908, **41**, 3966; 1909, **42**, 303; *Annalen*, 1911,

385, 117) and formulated as above by Lowry (*Trans. Faraday Soc.*, 1923, **19**, 488), supports this contention, as also does that of the α-phenylbenzylallylmethylammonium ion (VI) discovered by Pope and Peachey (J., 1899, **75**, 1127). From these considerations it therefore appears that the possession of a lone pair of electrons is in no way associated with the asymmetry under discussion, but that when a tercovalent atom is asymmetric, it must carry a positive charge.

Since the presence of this positive charge appears to be essential, the tercovalent atom cannot occupy the centre of the asymmetric system. It must be ex-centric; otherwise its presence would be immaterial, as is made obvious by a survey of compounds containing asymmetric quadricovalent atoms.

The hypothesis finally decided upon is therefore—that an atom can be asymmetric if it is attached to three dissimilar groups and carries a positive charge, *i.e.*, has lost an electron. Such an atom could be considered as occupying the apex of a tetrahedron, at the other three corners of which lie the three dissimilar groups (VII).

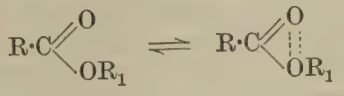
Essentially then, the hypothesis advanced is that of van 't Hoff (1878) when speculating on the stereochemical possibilities of nitrogen compounds in his " Ansichten über die organische Chemie," with the added proviso that the atom should bear a positive charge. Werner also (" Lehrbuch der Stereochemie," 1904, p. 317) has drawn a sharp distinction between the asymmetry of quadrivalent carbon compounds and that of the sulphur compounds of Pope and Peachey and Smiles. Werner considered that the system $M\begin{smallmatrix}R_1\\R_2\\R_3\end{smallmatrix}$ was asymmetric, the four atoms being at the corners of a tetrahedron, and that in the asymmetric sulphur (or selenium) compound the fourth group was co-ordinated with the sulphur atom.

The deduction that the tercovalent atom should be positively charged is of great interest, since it indicates that one valency electron (or possibly two) in the molecule is subjected to influences which may leave its companions unaffected. This might give rise to dissymmetry of the orbits or vibrational frequencies amongst the electrons of the molecule, assumptions which have been employed by physicists in theoretical studies of optical activity.

A Possible Cause of the Complex Rotatory Dispersion exhibited by Esters derived from Optically Active Secondary Alcohols and the n-*Aliphatic Carboxylic Acids.*

In Part V (J., 1914, **105**, 830) *et seq.* of these investigations it was suggested that the complex rotatory dispersion exhibited by the

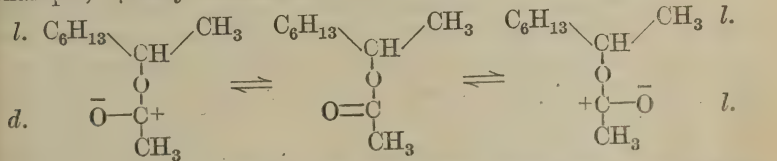
carboxylic esters of optically active secondary alcohols was due to the existence within the apparently homogeneous ester of two isodynamic forms possessing rotatory powers of opposite sign and different rotatory dispersive powers. As a preliminary hypothesis, the two isodynamic forms were written



being based on an alternative formula, $-C\lessdot^{OH}_{O}$, for the carboxyl group suggested by Smedley (J., 1909, **95**, 931).

Written as above, it is difficult to imagine why the isodynamic forms of the ester should have different signs of rotation, this being considered essential to account for the success with which the rotatory dispersion curves of these esters can be reproduced by Drude equations containing two terms of opposite sign.

If, however, the conclusion drawn in the preceding section is correct, an alternative formulation of the isomeric forms of carboxylic esters is possible which indicates, as in the case of sulphinic esters, that an additional centre of asymmetry may be present. For example, *l*-β-octyl acetate could be written



Thus the ester itself is to be considered capable of assuming an asymmetric structure in which the carbon atom of the carboxyl group is in combination with three different groups and is positively charged. This new asymmetric centre will, however, show, as far as our present ideas would lead us to expect, a fleeting and variable rotatory power, since the equilibrium (to which a one-sidedness is imparted under most conditions by the imposition on the molecule of that configuration with which the active octyloxy-group desires to be associated) could be rapidly readjusted by the addition or withdrawal of two oxygen electrons from the valency shell of the carbon atom. Such lability of activity is in agreement with the failure to detect any lag in the return of the rotatory powers of such esters to their original values after the presumed disturbance of the equilibrium between the three forms, or their suppression or modification, *e.g.*, by heat, solvation, etc.

The assumed existence of two enantiomorphous forms of a carboxylic ester together with a third form which is truly ketonic

receives some support from the observations of Sugden (*loc. cit.*), who finds that some anomaly in the usually accepted constitution of these esters is reflected in their parachors. It should be mentioned also that Lowry and Walker (*Nature*, 1924, **113**, 565) consider that chromophoric groups in asymmetric molecules, such as the ketonic group in camphor, exhibit " induced asymmetry." Further, Lowry and Cutter (this vol., p. 609) suggest that " the complex dispersion, which so often appears on passing from an optically-active alcohol to its esters, may be due to the development of a partial rotation of opposite sign in the carbonyl radical of the unsymmetrical molecule, just as in the case of camphor."

The Mutarotation of the p-*Toluenesulphinic Esters of* l-β-*Octanol and of* l-*Menthol.*

The mobility of the alkyl *p*-toluenesulphinates has been studied by an investigation of the *p*-toluenesulphinic esters of *l*-β-octanol and of *l*-menthol.

It was found that the *l*-β-octyl esters of *p*-toluenesulphinic acid, produced by the three methods outlined in a previous section, had rotatory powers of different magnitude. This can only be ascribed to the influence of the asymmetric acid radical. Thus when approximately molecular proportions of the *l*-alcohol and the sulphinyl chloride were allowed to react in ethereal solution and potassium carbonate was employed to remove the hydrogen chloride, the lævorotatory ester isolated had $\alpha_{\mathrm{D}}^{22^\circ}$ $-22{\cdot}0^\circ$. When pyridine was used in place of potassium carbonate, the rotatory power of the ester obtained was of the order $\alpha_{5461}^{25^\circ}$ $-6{\cdot}0^\circ$. Further, the ester obtained by the displacement of the ethoxy-group of ethyl *p*-toluenesulphinate had $\alpha_{5461}^{25^\circ}$ $-25{\cdot}0^\circ$.

When such esters had been twice distilled quickly, they could be redistilled slowly without more than traces of decomposition. Especially was this true of the ester prepared by the displacement method. It was found that when this ester was slowly redistilled it could be separated into fractions with widely different rotatory powers, indicating that *l*-β-octyl *l*-*p*-toluenesulphinate could be separated from *l*-β-octyl *d*-*p*-toluenesulphinate by fractional distillation at very low pressures.

A remarkable fact about such distillations was that, if the ester was redistilled slowly and as far as possible completely, its rotatory power increased by $\alpha_{5461}^{25^\circ}$ $-2{\cdot}0^\circ$. Indeed, by this means *l*-β-octyl *l* + *dl*-*p*-toluenesulphinate was obtained with $\alpha_{5461}^{25^\circ}$ $-68{\cdot}14^\circ$. This result suggests that during redistillation dextrorotatory *l*-β-octyl *d*-*p*-toluenesulphinate changes into lævorotatory *l*-β-octyl *l*-*p*-toluenesulphinate. When, however, *l*-β-octyl *l* + *dl*-*p*-toluene-

sulphinate was heated under the same low pressures used during these fractionations, but at temperatures just below those at which distillation occurred, its rotatory power was unaltered at the end of 2 hours. It is suggested tentatively, therefore, that the observed increase in rotatory power during slow distillation is due to the loss of a small quantity of dextrorotatory *l*-β-octyl *d*-*p*-toluenesulphinate which, having a higher boiling point, predominates in the ester moistening the flask at the end of the distillation. The evidence obtained from the experiment described, however, is not conclusive, since the ester did not pass through the vapour state before its rotatory power was redetermined.

On fractional distillation of a lævorotatory β-octyl *p*-toluenesulphinate, with $\alpha^{25^\circ}_{5461}$ — 5·86°, prepared directly from *l*-β-octanol by its interaction with *p*-toluenesulphinyl chloride in presence of pyridine, the extreme fractions had $\alpha^{25^\circ}_{5461}$ — 23·30° and $\alpha^{25^\circ}_{5461}$ + 15·28°, respectively, the dextrorotatory ester doubtless being *l*-β-octyl *d*+*dl*-*p*-toluenesulphinate.

The interconvertibility of *l*-β-octyl *d*-*p*-toluenesulphinate and *l*-β-octyl *l*-*p*-toluenesulphinate with rotations of opposite sign is suggested by the results of the distillations and rendered more probable by the marked mutarotation which the esters displayed. Indeed all specimens on keeping, even that with $\alpha^{25^\circ}_{5461}$ + 15·28°, eventually reached a constant value of approximately $\alpha^{25^\circ}_{5461}$ — 19·0°.

In Table I are recorded the changes in rotatory power with time of (A) an ester prepared from *l*-β-octanol and the sulphinyl chloride in presence of pyridine, and (B) an ester obtained by the displacement of the ethoxy-group of ethyl *p*-toluenesulphinate.

TABLE I.

Mutarotation of Lævorotatory p-*Toluenesulphinates of* l-β-*Octanol.*

A				B			
Time in hours.	$\alpha^{25^\circ}_{5893}$.	$\alpha^{25^\circ}_{5461}$.	$\alpha^{25^\circ}_{4359}$.	Time in hours.	$\alpha^{25^\circ}_{5893}$.	$\alpha^{25^\circ}_{5461}$.	$\alpha^{25^\circ}_{4359}$.
—	−5·98°	−7·56°	−12·16°	—	−21·16° *	—	—
91	6·46	7·74	12·93	96	20·98	−24·92°	−45·68°
236	7·86	9·28	15·82	221	20·46	24·38	43·70
405	11·94	14·20	25·42	341	19·88	24·30	43·42
570	15·58	18·24	33·04	530	18·62	22·34	40·22
666	16·38	19·28	33·84	676	17·82	21·44	38·88
787	16·36	19·36	35·84	839	16·82	20·44	36·96
912	16·06	19·60	35·36	1031	16·42	19·72	35·50
1121	16·08	19·54	35·50	1222	16·06	19·68	35·42
1433	16·04	19·66	35·20	1541	16·08	19·62	35·14

* $\alpha^{14^\circ}_{5893}$ not $\alpha^{25^\circ}_{5893}$.

The curves obtained by plotting the above data are of a complex character and do not agree with a monomolecular law. They have

not so far been submitted to mathematical analysis, since it is not yet known how far they represent only mutarotation (*i.e.*, interconversion of the dextrorotatory and lævorotatory forms of the ester) as distinct from hydrolysis, oxidation by contact with the air, and decomposition or polymerisation of the possible intermediate form or forms, during the prolonged period the esters were under observation. Such doubts have arisen because, on attempted redistillation of esters the rotatory powers of which have reached the equilibrium value, small quantities of β-octanol can be recovered prior to the obvious decomposition which generally ensues.

That oxidation alone could account for the observed mutarotation is a view which can be dismissed, as the rotatory power of the sulphonic ester (the most likely oxidation product) is but half that of the equilibrium mixture. Considerable experimental evidence in support of the view that some interconversion of the dextrorotatory and lævorotatory forms of the ester takes place is supplied by the mutarotation data of a dextrorotatory *p*-toluenesulphinate of *l*-β-octanol (*l*-β-octyl *d* + *dl*-*p*-toluenesulphinate) recorded in Table II.

TABLE II.

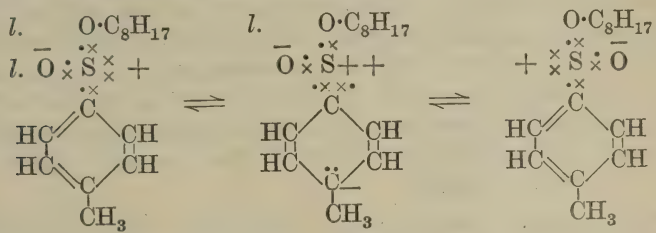
Mutarotation of a Dextrorotatory p-*Toluenesulphinate of* l-β-*Octanol.*

Time in hours.	$\alpha^{25^\circ}_{5893}$.	$\alpha^{25^\circ}_{5461}$.	$\alpha^{25^\circ}_{4359}$.	$n^{25^\circ}_{D}$.
—	+13·34°	+15·28°	+31·48°	1·5055
240	8·46	10·38	21·50	1·5052
408	2·44	3·18	8·14	1·5050
600	−10·34	−11·90	−20·98	1·5048
744	13·36	16·18	28·68	1·5047
911	15·96	19·36	34·56	—
935	—	—	—	1·5044
1106	16·28	19·50	35·06	1·5042
1443	15·84	19·12	34·12	1·5035

The preliminary experiments which have been made with the *p*-toluenesulphinyl derivative of *l*-menthol confirm and emphasise the correctness of the above conclusions. The lævorotatory modification of this ester has been prepared with a rotatory power in acetone solution ($c = 2{\cdot}5$) of $[\alpha]^{17^\circ}_{5461} - 240^\circ$, and the dextrorotatory modification with $[\alpha]^{17^\circ}_{5461} + 35^\circ$. The dextrorotatory form (*l*-menthyl *d* + *dl*-*p*-toluenesulphinate) was an oil which, after standing in a closed glass vessel for 91 days, changed to a crystalline mass of *l*-menthyl *l* + *dl*-*p*-toluenesulphinate with $[\alpha]^{17^\circ}_{5461} - 187{\cdot}6^\circ$.

The Mechanism of the Mutarotation.—The mechanism of the change *l*-β-octyl *d*-*p*-toluenesulphinate $\rightleftharpoons$ *l*-β-octyl *l*-*p*-toluenesulphinate is obscure, especially as it proceeds in the absence of solvents. This suggests that it is intramolecular in character and possibly is due to the valency shells of the atoms which make up

the ester being able to adopt an alternative configuration. This might occur by the sulphur atom sharing its " lone pair " of electrons with the carbon atom through which it is attached to the toluene ring. A readjustment of the valencies of that ring would ensue, leaving the para-carbon atom with a completed valency shell and therefore with a negative charge.* The sulphur atom would acquire an additional positive charge.

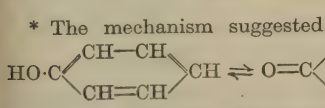


Such a mechanism would be impossible in either *l*-β-octyl benzoate † or *l*-β-octyl *p*-toluenesulphonate, in neither of which, nor indeed in any optically active benzoate or sulphonate, has mutarotation been detected. The suggested mechanism would also account for the observed racemisation of optically active ethyl *p*-toluenesulphinate.

The Optical Inversion of p-*Toluenesulphinic Esters which contain an Asymmetric Sulphur Atom.*

When lævorotatory β-octyl *p*-toluenesulphinate is prepared from molecular proportions of ethyl *p*-toluenesulphinate and *l*-β-octanol, it has $\alpha^{25°}_{5461} - 25°$. When two molecular proportions of the ethyl ester are used and one of *l*-β-octanol, it has $\alpha^{25°}_{5461} - 34°$ and the ethyl *p*-toluenesulphinate remaining is lævorotatory.

Further, the alcoholysis of a lævorotatory β-octyl *p*-toluenesulphinate with $\alpha^{25°}_{5461} - 36°$ gives a dextrorotatory ethyl *p*-toluene-

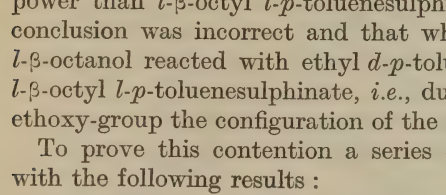
* The mechanism suggested differs from the tautomerism of phenol,  , which is indicated by the identity of benzoquinonemonoxime and *p*-nitrosophenol, and for which much other chemical evidence is reviewed by Ingold (J., 1922, **121**, 1139), only in the supposed absence of a mobile hydrogen atom. Its validity could of course be tested by an investigation of esters of alkyl-sulphinic acids when suitable methods have been found for the preparation of these compounds in a state of purity.

† The possibility that *l*-β-octyl benzoate does show slow mutarotation or that it can exist in two relatively stable modifications of opposite rotatory power is remote. Widely different methods have been used in this laboratory for its preparation, and it has been fractionally distilled without marked alteration in its rotatory power, which rapidly reached a constant value.

sulphinate and *l*-β-octanol. These two products apparently react to some extent while being separated by fractional distillation, giving a small quantity of a lævorotatory β-octyl *p*-toluenesulphinate with $\alpha^{25°}_{5461} - 62°$.

A consideration of these results led to the conclusion that if dextrorotatory ethyl *p*-toluenesulphinate has the " *d* " configuration, then *l*-β-octyl *d*-*p*-toluenesulphinate has a higher lævorotatory power than *l*-β-octyl *l*-*p*-toluenesulphinate. It was felt that this conclusion was incorrect and that what really occurred was that *l*-β-octanol reacted with ethyl *d*-*p*-toluenesulphinate and produced *l*-β-octyl *l*-*p*-toluenesulphinate, *i.e.*, during the displacement of the ethoxy-group the configuration of the ester molecule was reversed.

To prove this contention a series of reactions was carried out with the following results :



Thus, when *l*-β-octanol is heated with two molecular proportions of either ethyl or *n*-butyl *p*-toluenesulphinate, a lævorotatory normal ester is left in each case. The configuration of lævorotatory ethyl *p*-toluenesulphinate is therefore the same as that of lævorotatory *n*-butyl *p*-toluenesulphinate. The reaction between *n*-butyl alcohol and lævorotatory ethyl *p*-toluenesulphinate produces dextrorotatory *n*-butyl *p*-toluenesulphinate. Whilst considerable racemisation, due to the interaction or possibly to mutarotation, has taken place, yet it is clear that these reactions are also accompanied by inversion of configuration.

A Comparison between the p-*Toluenesulphinic and the* p-*Toluenesulphonic Esters of* l-β-*Octanol and of* l-*Menthol.*

In the same way that optically active ethyl *p*-toluenesulphinate when oxidised yields optically inactive ethyl *p*-toluenesulphonate, the oxidation of *l*-menthyl *l*+*dl*-*p*-toluenesulphinate and of *l*-menthyl *d* + *dl*-*p*-toluenesulphinate yields the same *l*-menthyl *p*-toluenesulphonate. Similarly, the oxidation of β-octyl esters of *p*-toluenesulphinic acid with widely different rotatory powers yields the same *l*-β-octyl *p*-toluenesulphonate.

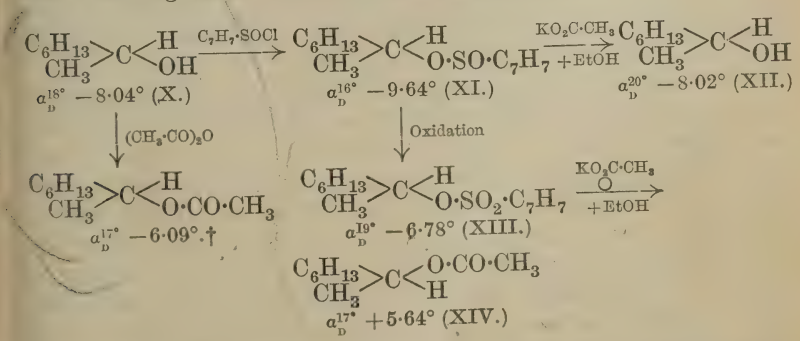
The asymmetric character of the *p*-toluenesulphinic esters does not appear, therefore, to be retained by those of *p*-toluenesulphonic acid.

There exists also a wide difference between the chemical characteristics of the two series of esters, attributable to the loss by the sulphur atom of the sulphinoxy-group of its unsaturated character when that group is converted into the sulphonoxy-group. For, when the sulphinic esters are refluxed with an ethyl-alcoholic solution of potassium acetate, they do not enter into reaction with the salt but, as described in the previous section, undergo alcoholysis (VIII). The sulphonic esters, however, under the same experimental conditions, react readily, not only with the ethyl alcohol to a small extent, but also to a larger extent with the potassium acetate (IX).

(VIII.) $\begin{matrix} RO \\ H \end{matrix}\!\!\uparrow\!\!\begin{matrix} SO\cdot C_7H_7 \\ OEt \end{matrix}$ $\qquad$ $\begin{matrix} R \\ OEt \\ CH_3CO_2 \end{matrix}\!\!\uparrow\!\!\begin{matrix} O\cdot SO_2\cdot C_7H_7 \\ H \\ K \end{matrix}$ (IX.)

The mode of decomposition of sulphinic esters indicated in (VIII) suggests that the four bonds of the carbon atom in the group RO would remain undisturbed, and hence any optically active alcohol regained by alcoholysis should be unchanged in sign or magnitude of rotatory power. In a reaction of a sulphonic ester such as is indicated in (IX) the bonds of the asymmetric carbon atom are disturbed and the asymmetric complex, of which the group R forms a part, would be likely to be inverted in configuration * or to suffer loss of rotatory power. These deductions are in agreement with the experimental results described below, obtained with (*a*) the *l*-β-octyl esters and (*b*) the *l*-menthyl esters of *p*-toluenesulphinic and of *p*-toluenesulphonic acids.

(a) *The* l-β-*Octyl Esters. The Optical Inversion of* l-β-*Octanol.*—The following series of reactions was carried out :



* The complete inversion of optically active benzylmethylcarbinol (Part XVII, J., 1923, **123**, 44) and of dextrorotatory ethyl lactate (Part XXIV, this vol., p. 399) have been effected by the aid of such reactions.

† Part V, J., 1914, **105**, 830.

l-β-Octanol (X) was converted into its *p*-toluenesulphinic ester by the requisite sulphinyl chloride in presence of pyridine, and since the reaction can be assumed to consist solely in the replacement of the hydrogen atom of the hydroxyl group of the *l*-alcohol by the *p*-toluenesulphinyl group, the valencies of the asymmetric carbon atom remain undisturbed and therefore the asymmetric carbon complex in the sulphinic ester (XI) has the same configuration as that of its parent alcohol.

When heated under reflux with an alcoholic solution of potassium acetate, the sulphinate (XI) was decomposed and *l*-β-octanol (XII), unchanged in rotatory power, was regenerated. The oxidation of the sulphinate to the sulphonate * (XIII) involves the addition of an oxygen atom to the sulphur atom and is unlikely to cause configurative change of the asymmetric carbon complex in the molecule. The *l*-sulphonate when treated in a similar manner to the *l*-sulphinate gave *d*-β-octyl acetate (XIV) with almost complete inversion of configuration. This is evident, since *l*-β-octanol, when treated with acetic anhydride, gives *l*-β-octyl acetate $\alpha_D^{17^\circ} - 6{\cdot}09^\circ$, from which by hydrolysis *l*-β-octanol can be regained unchanged in rotatory power.

These results have been confirmed by means of *d*-β-octyl *p*-toluenesulphonate and an ethyl-alcoholic solution of potassium benzoate, interaction of which led to the formation of *l*-β-octyl benzoate, $\alpha_D^{23^\circ} - 28{\cdot}7^\circ$, which gave on hydrolysis *l*-β-octanol, $\alpha_D^{23^\circ} - 6{\cdot}96^\circ$; and *l*-β-octyl ethyl ether, $\alpha_D^{23^\circ} - 14{\cdot}08^\circ$ as compared with $\alpha_D^{21{\cdot}5^\circ} + 15{\cdot}38^\circ$, the magnitude and sign of rotatory power of the ethyl ether prepared directly from *d*-β-octanol.

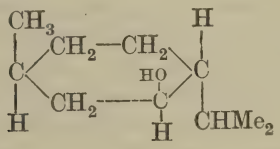
(b) *The* l-*Menthyl Esters. The Conversion of* l-*Menthol into* d-neo*Menthol*.—When a highly lævorotatory menthyl *p*-toluenesulphinate was heated under reflux with an alcoholic solution of potassium acetate, the *l*-menthol regenerated was optically pure.

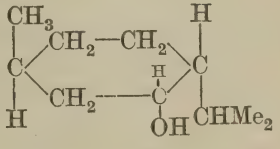
The *l*-menthyl *p*-toluenesulphonate required was prepared by the interaction of molecular proportions of *l*-menthol and *p*-toluenesulphonyl chloride in presence of pyridine, a mode of preparation which ensured that the *l*-menthyl complex would retain the configuration of the parent *l*-menthol. It reacted readily with salts of carboxylic acids in ethyl-alcoholic solution, but by far the greater part of the product was a menthene. Of the large number of experiments performed, only two gave decisive evidence of the formation of an ester of *d-neo*menthol, namely, the interaction of the sulphonic ester with glacial acetic acid and with ammonium

* It was found that *l*-β-octyl *p*-toluenesulphonate cannot readily be prepared by the direct interaction of the *p*-toluenesulphonyl chloride and the *l*-alcohol in presence of pyridine.

acetate. With acetic acid, a mixture of menthols with $\alpha_D^{17^\circ}$ $-28{\cdot}94^\circ$ was obtained, the hydrogen phthalic esters of which on recrystallisation gave an ester with $[\alpha]_D + 14{\cdot}60^\circ$, which was therefore mainly *d-neo*menthyl hydrogen phthalate (compare Pickard and Littlebury, J., 1912, **101**, 109). The recovered menthols on oxidation gave as the sole product an optically pure *l*-menthone with $[\alpha]_D^{20^\circ}$ $-24{\cdot}28^\circ$. When ammonium acetate was used, the mixture of menthols eventually isolated had $\alpha_D^{17^\circ} + 10{\cdot}0^\circ$.

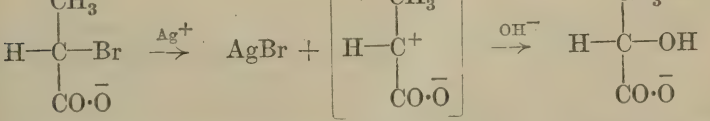
This conversion of *l*-menthol into *d-neo*menthol is not strictly a Walden inversion, since the chemical reactivities of these two alcohols are not identical and, moreover, they are not optical isomerides. They are geometric isomerides in which the hydrogen atom and the hydroxyl group are attached to an asymmetric carbon atom, the relationship between them being indicated by the following formulæ :





The Bearing on the Theory of the Walden Inversion of the Phenomena encountered during the Investigation.

The possible free existence of the system $+C\begin{matrix}R_1\\R_2\\R_3\end{matrix}$ in an optically active state is a deduction of particular interest from the point of view of the Walden inversion. After the experiments of Senter (J., 1910, **97**, 362) had shown that the reaction between halogen-substituted carboxylic acids and silver salts took place between the acid anion and the silver kation, Biilmann (*Annalen*, 1913, **388**, 338) tacitly assumed the free existence of such a system, formulating the hydroxylation of α-bromopropionic acid as follows :

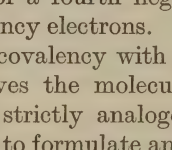


Whilst such a representation of this reaction cannot be advocated at present, it appears possible that the formation of an asymmetric system associated with a tercovalent carbon atom bearing a positive charge is connected with the phenomenon of the Walden inversion. On the current ideas of the electronic theory of valency and those of the classical theories of stereochemistry, it would appear that such

a system would not be inverted in configuration by its conversion into a quadricovalent one through the addition of a negative ion. The conclusion seems inevitable, therefore, that if the production of such a system represents an intermediate stage in a reaction leading to a Walden inversion, it must at the moment of its formation adopt the opposite configuration to that of the quadricovalent system from which it arose.

It is convenient, in the light of the above observations, to consider the inversion of the *p*-toluenesulphinic esters which occurs during alkyloxy-interchange. The fact that *l*-β-octanol can be recovered unchanged either in sign or magnitude of rotatory power from its *p*-toluenesulphinic esters is strong evidence that during the inversion the *l*-octyloxy-group leaves the molecule.

At first sight it would appear that a mechanism for the inversion could readily be formulated, since the sulphur atom is attached to only three groups. The electronic theory of valency, however, forbids the addition of a fourth negative group, since that would cause a surplus of valency electrons. Since from the theory a fourth group cannot form a covalency with the sulphur atom until one of the three groups leaves the molecule, the inversion of sulphinic esters appears to be strictly analogous to the Walden inversion. It is of course possible to formulate an intermediate complex such as,



but unless some subdivision of valencies occurs, it would appear that just as in the case of quadricovalent atoms Biilmann (*loc. cit.*) was forced to assume that their conversion into tercovalent atoms did not entail loss of asymmetry, so also it is necessary from the above-mentioned considerations to assume that a sulphinic ester can lose its alkyloxy-group and the residual system can remain asymmetric.

Indeed, a careful consideration of both the Walden inversion and the analogous optical inversion of *p*-toluenesulphinic esters indicates that such inversions are intimately connected with the withdrawal of a negative group from an asymmetric molecule and in particular with the withdrawal of two electrons from the valency shell of the atom usually designated as asymmetric.

Experimental.

p-*Toluenesulphinic acid* was prepared by reducing recrystallised *p*-toluenesulphonyl chloride by a strong solution of sodium sulphite

(Blomstrand, *Ber.*, 1870, **3**, 965), and purified by recrystallising its sodium salt from water; the acid obtained from the pure sodium salt was partly dried on a porous plate and then completely dried by prolonged desiccation over calcium chloride in a vacuum.

p-*Toluenesulphinyl chloride* was prepared when required by Hilditch and Smiles' method (*Ber.*, 1908, **41**, 4113; Hilditch, J., 1910, **97**, 2585). Thionyl chloride * (1·1 mols.) was dissolved in an equal volume of dry ether, and the acid (1 mol.) added gradually with agitation. When all the acid had dissolved, the mixture was warmed very gently until gases were no longer evolved. The ether and the excess thionyl chloride were then removed in a vacuum at the ordinary temperature, and the oily residue was dissolved in light petroleum. The solution thus obtained was filtered from the small quantity of a white solid which was usually precipitated, and subjected to a vacuum at the ordinary temperature for at least 6 hours; the *p*-toluenesulphinyl chloride then remained as a pale yellow oil.

This acid chloride was described by Hilditch and Smiles (*loc. cit.*) as a solid, m. p. 55—58°, but Braun and Kaiser (*Ber.*, 1923, **56**, 553) were unable to crystallise a specimen which had been distilled.

Ethyl dl-p-*Toluenesulphinate.*—A vigorous evolution of carbon dioxide occurred when *p*-toluenesulphinyl chloride (172 g.) in ether (100 c.c.) was added to a mixture of ethyl alcohol (69 g.) and ether (300 c.c.) covering anhydrous potassium carbonate (207 g.). After 12 hours, water was added, and the ethereal layer was separated, repeatedly washed with water, and dried over potassium carbonate. On removal of the ether, 115 g. of crude ethyl *dl-p*-toluenesulphinate were obtained which, when distilled at 0·1 mm., darkened considerably but gave a colourless distillate, 95 g., b. p. 99—104°, $n_D^{25°}$ 1·5306, and left a black, tarry residue, 12 g., which did not distil at a higher temperature and deposited crystals on cooling.

In order to test the purity and homogeneity of the ethyl *dl-p*-toluenesulphinate, it was slowly redistilled at less than 0·1 mm.,† and divided into eight fractions. Six of these, of combined weight 75 g., had $n_D^{25°}$ 1·5309, whilst redistillation of the extreme fractions

* The thionyl chloride used was water-white in appearance, having been successively distilled from quinoline, linseed oil, and beeswax (Meyer and Schlegel, *Monatsh*, 1913, **34**, 569).

† A Fleuss pump backing a Langmuir mercury-vapour pump was employed throughout this research to obtain the pressure given as "less than 0·1 mm." As a rough gauge to the low pressures obtained, a discharge tube was employed. With the distillation flask cut off from the pumps, a very high vacuum could be obtained, but during distillation the actual pressure in the distillation flask, and hence the boiling point of the liquid distilled was influenced by slight leakages and by the presence of restrictions, *e.g.*, taps of narrow bore, in the connexions to the various distillation flasks and apparatus used.

yielded a further 13·5 g. with the same refractive index. It was therefore concluded that ethyl *dl*-*p*-toluenesulphinate with $n_D^{25°}$ 1·5309 was pure and was not a mixture of isomerides of widely different chemical constitutions. It had $d_4^{25°}$ 1·114 (Found: S, 17·3. $C_9H_{12}O_2S$ requires S, 17·4%).

Ethyl *dl*-*p*-toluenesulphinate was also prepared by the action at — 10° of *p*-toluenesulphinyl chloride (1 mol.) on ethyl alcohol (1 mol.) dissolved in light petroleum (200 c.c.) containing pyridine (1 mol.). The action was complete after 2 hours. The solution was washed four times with water, twice with dilute hydrochloric acid, and again with water, dried with anhydrous potassium carbonate, the light petroleum removed, and the product distilled as previously described. It left a larger non-volatile residue, but the distillate was identical with that previously described.

The Determination of the Parachor of Ethyl dl-p-*Toluenesulphinate* (communicated by Dr. S. Sugden).

TABLE III.

t.	Pressure, dyn./cm.².	*D*, g./c.c.	ϕ.	γ, dyn./cm.	Parachor. $\gamma^{1/4}M/D$.
18°	4849	1·120	1·0217	38·48	409·4
32	4662	1·107	1·0224	37·03	410·3
49·5	4432	1·091	1·0232	35·23	411·1

Densities determined: $d_4^{18·5°}$ 1·120, $d_4^{35°}$ 1·105, $d_4^{50·5°}$ 1·090, whence $d_4^{t°} = 1·137 - 0·000935t$. The surface-tension measurements were made in apparatus 4, for which $r_2 = 0·139$ cm. and $A = 0·007767$. For the method of calculation, see J., 1922, **121**, 858; 1924, **125**, 27; and for the values of the atomic parachors, see J., 1924, **125**, 1180.

n-*Butyl* dl-p-*toluenesulphinate* was prepared by the interaction of *n*-butyl alcohol and *p*-toluenesulphinyl chloride in ethereal solution in presence of potassium carbonate. After two fractionations at a low pressure, 80% of the crude ester was obtained with b. p. 90—95°/0·1 mm., $n_D^{25°}$ 1·5195, and $d_4^{25°}$ 1·066 (1·1378 required 0·3005 of potassium hydroxide for complete hydrolysis. Theory, 0·3008).

The p-*Toluenesulphinic Esters of Optically Active* β-*Octanol. The Methods of Preparation employed and the Mutarotation shown by the Esters obtained.*

(a) *By the Interaction of* l-β-*Octanol and* p-*Toluenesulphinyl Chloride in Ethereal Solution in Presence of Potassium Carbonate.*— To potassium carbonate (30 g.), covered by a solution of *l*-β-octanol ($\alpha_D^{21°}$ — 8·10°; $l = 1·0$) (16 g.) in ether (25 c.c.), *p*-toluenesulphinyl chloride (26 g.) in ether (25 c.c.) was added; the mixture was left

for 4 days and occasionally stirred. Water was then added, the ethereal layer separated, washed with water, and dried over potassium carbonate. After removal of the ether, the crude β-octyl *p*-toluenesulphinate was distilled at less than 0·1 mm. It had b. p. 125—128° and left a black tarry residue. On redistillation, β-octyl *p*-toluenesulphinate (25 g.) was obtained as a colourless oil with $n_D^{20°}$ 1·5065 and $\alpha_D^{22°}$ — 22·16 ($l = 1·0$). 1·3304 required 0·2780 of potassium hydroxide for complete hydrolysis (theory, 0·2784).

Mutarotation. The ester was stored in a glass bottle. Its rotatory power ($l = 0·5$) became $\alpha_D^{19°}$ — 8·28° after 360 hours, $\alpha_D^{21°}$ — 8·21° after 792 hours, $\alpha_D^{18°}$ — 8·01° after 1608 hours, and $\alpha_D^{20°}$ — 7·88°, $\alpha_{5461}^{20°}$ — 9·75°, $\alpha_{4359}^{20°}$ — 17·08° after 2376 hours; $n_D^{20°}$ 1·5053.

Reaction with glacial acetic acid. 9·5972 G. of the ester were made up to 100 c.c. with glacial acetic acid which had been previously distilled from potassium permanganate. The solution was immersed in a thermostat at 25·15° and the following determinations of its rotatory power were taken at 25° in a 2-dcm. tube :

TABLE IV.

Time (hours)	0	74	142	241	335	425	570	739
$\alpha_{5893}^{25°}$	−4·27°	−1·03°	−0·54	−0·37°	−0·29°	−0·31°	−0·27°	−0·27°
$\alpha_{5461}^{25°}$	5·23	1·35	0·71	0·50	0·40	0·42	0·35	0·34
$\alpha_{4359}^{25°}$	9·28	2·26	1·04	0·59	0·52	0·55	0·44	0·53

After the last reading had been taken, the solution was poured into water, and the oil which separated extracted with ether. The ethereal extract was washed with water until free from acid and then dried over anhydrous sodium sulphate. On removal of the ether, the residue was distilled, when it gave a fraction, b. p. 89—90°/17 mm. (5 g.), which was *l*-β-octyl acetate. A black, viscous residue remained which decomposed on attempted distillation at a pressure less than 0·1 mm. The *l*-β-octyl acetate was redistilled and then had $d_4^{25°}$ 0·8570, $\alpha_D^{14·5°}$ — 6·00°, $\alpha_{5461}^{14·5°}$ — 7·14°, values in close agreement with those given in Part V (*loc. cit.*).

Assuming that the lævorotatory β-octyl *p*-toluenesulphinate was converted completely into *l*-β-octyl acetate, 6·16 g. of the acetate were produced and $[\alpha]_D^{25°}$ —2·27° would represent its specific rotatory power in solution. In Part V (*loc. cit.*), $[\alpha]_D^{20°}$ — 3·65° is given for the specific rotatory power of *l*-β-octyl acetate in acetic acid solution ($c = 5$), and hence it is possible that at the end of the experiment the solution contained some other optically active ingredient which did not contain the β-octyl radical.

(b) *By the Interaction of* l-β-*Octanol and* p-*Toluenesulphinyl Chloride in Presence of Pyridine.*—To a solution of *l*-β-octanol ($\alpha_D^{22°}$ — 8·06°; $l = 1·0$) (12 g.) in pyridine (10 g.) cooled to — 17°,

p-toluenesulphinyl chloride (17 g.) was added gradually so that the temperature did not rise above 0°. After 12 hours, the product was poured into water, from which the oil which separated was extracted with ether. The ethereal extract was thoroughly washed with water, then with dilute hydrochloric acid, and again with water. It was then dried over potassium carbonate, the ether removed by distillation, and the residue, lævorotatory β-octyl *p*-toluenesulphinate, distilled at less than 0·1 mm.; 4 g. of *l*-β-octanol were recovered from the crude ester during the distillation, and after the ester itself had been distilled a small tarry residue, 0·5 c.c., remained in the flask. The lævorotatory β-octyl *p*-toluenesulphinate after a rapid redistillation at less than 0·1 mm. weighed 12 g. and had $n_D^{25°}$ 1·5052 (1·0917 required 0·2294 of potassium hydroxide for complete hydrolysis. Theory, 0·2279).

Mutarotation. The ester, in a glass container, was placed in a thermostat at 25·15°, and observations of its rotation in a tube of 50 mm. at 25° were made at intervals. The rotatory power is recorded as for a tube of 100 mm. in Table I (p. 2561).

After 1435 hours, the ester was dissolved in ether, the solution washed with dilute potassium carbonate solution to remove possible traces of acidic substances, and, after drying with anhydrous potassium carbonate, the ester was recovered in the usual manner and distilled in a high vacuum. It darkened rapidly and gave a low-boiling fraction which from its odour contained β-octanol. The main bulk of the ester, however, distilled at 105—110° and had $n_D^{25°}$ 1·5044, $\alpha_{5893}^{25°}$ — 11·64°, $\alpha_{5461}^{25°}$ — 14·03°, and $\alpha_{4359}^{25°}$ — 25·68 ($l = 0·5$).

A black residue which would not distil without decomposition remained in the distillation flask.

(c) *By the Displacement of the Ethoxy-group of Ethyl* dl-p-*Toluenesulphinate by heating that Ester with* l-β-*Octanol.*—*l*-β-Octanol ($\alpha_D^{18°}$ — 8·04°; $l = 1·0$) (9 g.) and ethyl *dl-p*-toluenesulphinate (12·7 g.) were mixed and heated in a flask maintained at 15 mm. on a steam-bath. After 54 hours, the product was distilled rapidly at less than 0·1 mm. Lævorotatory β-octyl *p*-toluenesulphinate (16 g.) was obtained, b. p. 122—124°, $n_D^{19°}$ 1·5078, and $\alpha_D^{14°}$ — 21·16° ($l = 1·0$).

Mutarotation. The ester was placed in a glass bottle immersed in a thermostat at 25·15°. Determinations of its rotatory power in tubes of 50 mm. were made at intervals at 25° and are recorded as for 100 mm. tubes in Table I (p. 2561).

After 1540 hours, the ester, the rotatory power of which had reached apparently a constant value, was distilled in a high vacuum. Three drops of distillate, having an odour resembling that of β-octanol, were obtained before the temperature of the vapours leaving the distillation flask reached 120°. The ester darkened rapidly, but

about half of it was distilled before the residue showed marked signs of decomposition. This distillate had $n_D^{25°}$ 1·5005; $d_4^{25°}$ 1·000; $\alpha_{5893}^{25°}$ — 13·52°, $\alpha_{5461}^{25°}$ — 16·25°, and $\alpha_{4359}^{25°}$ — 30·09° ($l = 0·5$).

Mutarotation of the ester in benzene solution. The lævorotatory ester used was prepared from *l*-β-octanol ($\alpha_D^{22°}$ — 8·06°; $l = 1·0$) as previously described in this section. It was redistilled at less than 0·1 mm. and had b. p. 123—125° and $\alpha_D^{20°}$ — 24·72° ($l = 1·0$). 8·5294 G. were made up to 100 c.c. with pure benzene which had been distilled from phosphorus pentoxide. The glass flask containing the solution was placed in a thermostat at 25·15°. The specific rotatory powers given below were calculated from the rotatory powers observed in a 2-dcm. tube at 25°.

TABLE V.

Time (hours)	0	62	256	431	598	763	911	1073	1241
$[\alpha]_{5893}^{25°}$	−27·8°	−27·6°	−27·2°	−19·2°	−15·6°	−13·3°	−13·3°	−13·4°	−13·6°
$[\alpha]_{5461}^{25°}$	33·3	32·9	32·6	22·3	18·7	15·8	16·0	15·9	16·0
$[\alpha]_{4359}^{25°}$	61·1	60·5	60·1	40·9	33·3	28·1	28·4	29·5	29·0

After the last recorded determination had been made, the solution was placed in contact with anhydrous sodium sulphate for 12 hours. The benzene was then removed in a vacuum at the ordinary temperature. The recovered ester was yellow and had $n_D^{25°}$ 1·5034, $\alpha_{5893}^{25°}$ — 7·46°, and $\alpha_{5461}^{25°}$ — 8·76° ($l = 0·5$); values approximating to those reached by the homogeneous ester on standing. An attempt was made to distil this ester in a high vacuum, but it darkened rapidly and decomposed after a few drops of distillate had been obtained.

The Fractional Distillation of the l-β-*Octyl Esters of* p-*Toluenesulphinic Acid.*—(a) *Isolation of* l-β-*octyl* l + dl-p-*toluenesulphinate.* Owing to the unstable nature of the crude *p*-toluenesulphinic esters, revealed during their first distillation, it was the usual practice in the early stages of this work to redistil them as rapidly as possible and attribute any observed change of boiling point to a change in the rate of distillation. Later, however, for reasons which have already been given, the distillations subsequent to the first were conducted very slowly in small flasks the necks of which were indented to ensure more efficient fractionation.

Lævorotatory β-octyl *p*-toluenesulphinate ($d_4^{25°}$ 1·009; $\alpha_{5893}^{20°}$ — 12·36°; $l = 0·5$) (18 g.), prepared from ethyl *dl*-*p*-toluenesulphinate and *l*-β-octanol ($\alpha_D^{22°}$ — 8·06°; $l = 1·0$) by the method of alkyloxy-interchange, was redistilled in this manner and divided during an experiment lasting 8 hours into four fractions with b. p.'s from 118 to 126° at less than 0·1 mm. Fraction I (6 g.) had $\alpha_{5461}^{25°}$ — 20·39° ($l = 0·5$); fraction II (6 g.), $\alpha_{5461}^{25°}$ — 18·32° ($l = 0·5$); fraction III (2 g.), $\alpha_{5461}^{25°}$ — 12·51° ($l = 0·5$); and fraction IV (2 g.), $\alpha_{5461}^{25°}$ — 3·5° ($l = 0·5$).

With the exception of fraction IV, these fractions were systematically refractionated into fractions (*a*) 5 g., $\alpha^{25^\circ}_{5461}$ — 23·22° ($l = 0{\cdot}5$); (*b*) 4 g., $\alpha^{25^\circ}_{5461}$ — 21·99° ($l = 0{\cdot}5$); (*c*) 3 g., $\alpha^{25^\circ}_{5461}$ — 16·42° ($l = 0{\cdot}5$); and (*d*) 2 g., $\alpha^{25^\circ}_{5461}$ — 8·41° ($l = 0{\cdot}5$). Fractions (*a*) and (*b*) were mixed and distilled slowly until 6 g. of distillate had been obtained. This distillate had $\alpha^{25^\circ}_{5461}$ — 26·81° ($l = 0{\cdot}5$). Fraction (*c*), after it had been distilled slowly and as far as possible completely, had $\alpha^{25^\circ}_{5461}$ — 18·24° ($l = 0{\cdot}5$). It was mixed with fraction (*d*) and the residue from the redistillation of fractions (*a*) and (*b*), and the whole was redistilled slowly and completely. The distillate had $\alpha^{25^\circ}_{5461}$ — 20·01° ($l = 0{\cdot}5$). After two more distillations, its rotatory power was $\alpha^{25^\circ}_{5461}$ — 23·80° ($l = 0{\cdot}5$). It was again redistilled and then added to the fraction with $\alpha^{25^\circ}_{5461}$ — 26·81° ($l = 0{\cdot}5$) (obtained as previously described by the fractionation of fractions *a* and *b*. The mixture was distilled three times; at the very low pressure used during the last redistillation, it had b. p. 94—102°, and the distillate $\alpha^{25^\circ}_{5461}$ — 30·6°, $\alpha^{25^\circ}_{4359}$ — 57·75° ($l = 0{\cdot}5$). The increase in the rotatory power of the ester when slowly and as far as possible completely redistilled continued, for after it had been redistilled three times it had $\alpha^{25^\circ}_{5893}$ — 28·24°, $\alpha^{25^\circ}_{5461}$ — 34·07°, and $\alpha^{25^\circ}_{4359}$ — 63·89° ($l = 0{\cdot}5$). It was then divided into two portions by a slow distillation. The distillate, b. p. 98—102°, had $n^{25^\circ}_{\mathrm{D}}$ 1·5051 and $\alpha^{25^\circ}_{5461}$ — 41·52°, $\alpha^{25^\circ}_{4359}$ — 78·20°; the residual ester in the flask had $\alpha^{25^\circ}_{5461}$ — 25·82° and $\alpha^{25^\circ}_{4359}$ — 48·07° ($l = 0{\cdot}5$).

The residual ester was heated for 2 hours at 125—130° under the pressure at which the distillations described above were performed. Care was taken that no distillation occurred. The rotatory power of the residual ester, now slightly charred, was $\alpha^{25^\circ}_{5461}$ — 25·62°, $\alpha^{25^\circ}_{4359}$ — 48·05° ($l = 0{\cdot}5$). It was then distilled, added to the distillate with $\alpha^{25^\circ}_{5461}$ — 41·52°, and the mixture redistilled; the *l*-β-octyl *l* + *dl*-*p*-toluenesulphinate then obtained had $n^{25^\circ}_{\mathrm{D}}$ 1·5051, $d^{25^\circ}_{4}$ 1·010, $\alpha^{25^\circ}_{5893}$ — 29·45°, $\alpha^{25^\circ}_{5461}$ — 35·13°, and $\alpha^{25^\circ}_{4359}$ — 66·39° ($l = 0{\cdot}5$).

Mutarotation. The ester with $\alpha^{25^\circ}_{5461}$ — 35·13° ($l = 0{\cdot}5$) was placed in a glass container in a thermostat at 25·15°, and its rotatory power was determined at intervals of 188 hours. For at least 762 hours its rotatory power was constant, but after 860 hours it had $n^{25^\circ}_{\mathrm{D}}$ 1·5039; $\alpha^{25^\circ}_{5893}$ — 8·46°, $\alpha^{25^\circ}_{5461}$ — 9·95°, and $\alpha^{25^\circ}_{4359}$ — 18·04° ($l = 0{\cdot}5$).

(b) *The isolation of* l-β-*octyl* d + dl-p-*toluenesulphinate.* The lævorotatory β-octyl *p*-toluenesulphinate used in this experiment was obtained by the gradual addition of *p*-toluenesulphinyl chloride (38 g.) to a solution of *l*-β-octanol ($\alpha^{22^\circ}_{\mathrm{D}}$ — 8·06°; $l = 1{\cdot}0$) (25 g.) in pyridine (22 g.), the temperature of the reaction mixture being maintained below 0°. The ester, isolated as previously described, was treated in ethereal solution with " norit " prior to its distillation,

at the commencement of which less than 1 g. of *l*-β-octanol was recovered; no attempt was made to separate any other low-boiling fraction after this had been removed. The distillate, b. p. up to 112° (38 g.), had $n_D^{25°}$ 1·5015, $d_4^{25°}$ 1·002, and $\alpha_{5893}^{25°}$ — 2·55°, $\alpha_{5461}^{25°}$ — 2·93° and $\alpha_{4379}^{25°}$ — 4·76° ($l = 0·5$). On redistillation, the distillate (35 g.), which left a small, tarry residue, had $n_D^{25°}$ 1·5004, $d_4^{25°}$ 1·002, and $\alpha_{5893}^{25°}$ — 3·14°, $\alpha_{5461}^{25°}$ — 3·73°, $\alpha_{4359}^{25°}$ — 5·27° ($l = 0·5$) (Found: S, 12·1. $C_{12}H_{24}O_2S$ requires S, 11·95%), but there had been an interval of 4 days between the determination of the rotatory power of the first distillate and that of the redistilled ester.

27 G. of this ester were then slowly redistilled and collected in two fractions. Fraction I (14 g., b. p. 99—105°, had $n_D^{25°}$ 1·4966, $d_4^{25°}$ 0·9968, $\alpha_{5893}^{25°}$ — 9·50°, and $\alpha_{5461}^{25°}$ — 11·65° ($l = 0·5$). It was yellow and somewhat impure (Found: S, 11·5%). Fraction II (9·3 g.), b. p. 105—114°, was colourless; it was *l*-octyl *d* + *dl*-*p*-toluenesulphinate with $n_D^{25°}$ 1·5055, $d_4^{25°}$ 1·005, $\alpha_{5893}^{25°}$ + 6·67°, $\alpha_{5461}^{25°}$ + 7·64°, and $\alpha_{4359}^{25°}$ + 15·74° ($l = 0·5$) (Found: S, 12·1%).

Mutarotation. The dextrorotatory ester was placed in a glass bottle in a thermostat at 25·15°, and the determinations of its rotatory power given in Table II (p. 2562) were made in a 50 mm. tube at 25°, but are given as for a tube of 100 mm.

The p-*Toluenesulphinic Esters of* l-*Menthol.*

(a) *Preparation of* l-*Menthyl* l + dl-p-*Toluenesulphinate.*—*l*-Menthol (18·3 g.) and ethyl *dl*-*p*-toluenesulphinate (21·6 g.) were heated together at about 60°/15 mm. After 48 hours, the product was cooled; it then solidified, and was readily soluble in benzene, ether, light petroleum, ethyl acetate, or acetone, but could be crystallised from the last four of these.

On recrystallisation from light petroleum, lævorotatory menthyl *p*-toluenesulphinate was obtained in fine needles, m. p. 98—100° and with $[\alpha]_{5893}^{17°}$ — 177·2°, $[\alpha]_{5461}^{17°}$ — 213·0°, $[\alpha]_{4359}^{17°}$ — 387·4° in acetone solution ($c = 2·483$, $l = 2·0$). After it had been recrystallised three times from aqueous acetone, subsequent recrystallisation from this solvent and also from light petroleum produced no further change in the ester, which had m. p. 108—109°; $[\alpha]_{5461}^{17°}$ — 239·9°, $[\alpha]_{4359}^{17°}$ — 433·8° in solution in acetone ($c = 2·609$, $l = 2·0$). It is considered that this ester was probably optically pure *l*-menthyl *l*-*p*-toluenesulphinate (0·5888 required 0·1141 of potassium hydroxide for complete hydrolysis. Theory, 0·1123).

Oxidation. To 1 g. of *l*-menthyl *l* + *dl*-*p*-toluenesulphinate in acetone (50 c.c.), finely ground potassium permanganate together with an equivalent quantity of magnesium sulphate was added until the pink coloration persisted for 15 minutes. The mixture was

diluted with water, and the manganese mud dissolved by passing sulphur dioxide; on cooling, the supernatant oil crystallised. The crystals, *l*-menthyl *p*-toluenesulphonate, after being washed with water and dried, had m. p. 96° (alone, or mixed with an authentic specimen), and $[\alpha]_{5893}$ — 69·0° in chloroform solution ($c = 2{\cdot}009$, $l = 2{\cdot}0$) (compare Hilditch, J., 1911, **99**, 233).

Mutarotation Phenomena Observed during the Preparation of l-*Menthyl* l + dl-p-*Toluenesulphinate*.—The filtrate from the first recrystallisation of the crude lævorotatory *l*-menthyl *p*-toluenesulphinate was concentrated and then cooled in a freezing-mixture; few crystals separated. The remaining solvent was therefore removed by distillation, finally at 15 mm.; the oily residue had $[\alpha]^{17°}_{5461}$ — 13·10° in acetone ($c = 7{\cdot}897$, $l = 2{\cdot}0$). Kept in a vacuum (0·1 mm.), it gradually became more viscous and set to a crystalline mass after 4 days. The fine needles, m. p. 100—104°, obtained by recrystallisation from acetone, had $[\alpha]^{17°}_{5461}$ — 224·9° in acetone ($c = 2{\cdot}790$, $= 2{\cdot}0$). A few drops of water were added to the filtrate from these crystals, when a further crop was obtained with m. p. 99—104°, and $[\alpha]^{17°}_{5461}$ — 228·0° in acetone ($c = 2{\cdot}780$, $l = 2{\cdot}0$). The mother-liquor from this recrystallisation was highly lævorotatory. From these observations it can be concluded that the lævorotatory power of the menthyl *p*-toluenesulphinate had increased considerably on standing, in agreement with the hypothesis that *l*-menthyl *d*-*p*-toluenesulphinate can change into *l*-menthyl *l*-*p*-toluenesulphinate.

These results were confirmed by a similar experiment in which *l*-menthol (49·2 g.) and ethyl *dl*-*p*-toluenesulphinate (58 g.) were allowed to react as previously described for 24 hours. The crude lævorotatory menthyl *p*-toluenesulphinate obtained had $[\alpha]^{17°}_{5461}$ — 82·4° in acetone ($c = 2{\cdot}670$, $l = 2{\cdot}0$). After crystallisation from aqueous acetone, *l*-menthyl *l* + *dl*-*p*-toluenesulphinate (30 g.) with m. p. 99—102°, and $[\alpha]^{17°}_{5461}$ — 235·6° in acetone ($c = 2{\cdot}430$, $l = 2{\cdot}0$), was obtained; after removal of the solvent from the mother-liquor, first by distillation and then in a vacuum, an oily menthyl *p*-toluenesulphinate was obtained with $[\alpha]^{17°}_{5461}$ — 18·8°, $[\alpha]^{17°}_{4359}$ — 29·2° in acetone ($c = 3{\cdot}243$, $l = 2{\cdot}0$). To remove possible traces of *l*-menthol, it was steam-distilled for 15 minutes; the residual oil, isolated and dried in ether, had $[\alpha]^{17°}_{5461}$ — 18·0°, $[\alpha]^{17°}_{4359}$ — 26·2° in acetone ($c = 2{\cdot}863$, $l = 2{\cdot}0$). The crystalline mass obtained by keeping it in a closed glass vessel for 84 days had $[\alpha]^{17°}_{5461}$ — 187·9°, $[\alpha]^{17°}_{4359}$ — 340·0° in acetone ($c = 2{\cdot}838$, $l = 2{\cdot}0$).

(b) *Preparation of* l-*Menthyl* d + dl-p-*Toluenesulphinate*.—A solution of *l*-menthol (15·6 g.) in pyridine (10 g.) was cooled to — 10°, and *p*-toluenesulphinyl chloride (17·2 g.) added in small quantities; after 12 hours, water was added, and the liberated oil extracted

washed, and dried in ether in the usual way. The oil, on cooling after removal of the solvent, deposited crystals (12 g.) which, separated by filtration, had $[\alpha]^{17°}_{5461}$ — 162·0° in acetone (c = 2·824, l = 2·0) and after recrystallisation from light petroleum gave *l*-menthyl *l* + *dl*-*p*-toluenesulphinate (7 g.), m. p. 102—103°; $[\alpha]^{17°}_{5461}$ — 227·1° in acetone (c = 2·566, l = 2·0).

The dark yellow oil, *l*-menthyl *d* + *dl*-*p*-toluenesulphinate, which had been filtered from the crystals had $\alpha^{17°}_{5461}$ + 10·0° (l = 0·25), the reading being accurate to 1°, and when dissolved in acetone had $[\alpha]^{17°}_{5461}$ + 35·04, $[\alpha]^{17°}_{4359}$ + 76·38° (c = 2·782, l = 2·0). It decomposed at about 190°/0·05 mm.

Oxidation of l-*menthyl* d + dl-p-*toluenesulphinate.* 1 G. of the ester when oxidised as previously described gave a crystalline *l*-menthyl *p*-toluenesulphonate which, after recrystallisation from ethyl alcohol, weighed 0·85 g., had m. p. 96°, and $[\alpha]^{17°}_{5893}$ — 69·1° in chloroform (c = 2·366, l = 2·0).

Mutarotation of l-*menthyl* d + dl-p-*toluenesulphinate.* 4·3 G. of the ester, kept in a closed glass tube for 91 days, became crystalline ($[\alpha]^{17°}_{5461}$ — 187·6°, $[\alpha]^{17°}_{4359}$ — 338·6° in acetone; c = 2·503, l = 2·0) and therefore were now chiefly composed of *l*-menthyl *l*-*p*-toluenesulphinate. On recrystallisation from aqueous acetone, *l*-menthyl *l* + *dl*-*p*-toluenesulphinate (3·5 g.) was obtained, m. p. 107°; $[\alpha]^{17°}_{5461}$ — 237·5° in acetone (c = 2·187, l = 2·0), and this, on oxidation by the method previously described, gave a theoretical yield of *l*-menthyl *p*-toluenesulphonate, m. p. 96°; $[\alpha]^{17°}_{5893}$ — 69·3° in chloroform (c = 2·430, l = 2·0).

Preparation of Optically Active Derivatives of p-*Toluenesulphinic Acid which do not contain an Asymmetric Carbon Atom.*

(a) *Lævorotatory Ethyl* p-*Toluenesulphinate* (*Ethyl* l + dl-p-*toluenesulphinate*).—*l*-β-Octanol ($\alpha^{22°}_{D}$ — 8·06°; l = 1·0) (12 g.; 1 mol.) and freshly prepared ethyl *dl*-*p*-toluenesulphinate ($n^{25°}_{D}$ 1·5309) (34 g.; 2 mols.) were heated at about 60°/16 mm. and then at 40° at a lower pressure for a further 2 hours. The product was systematically fractionated at less than 0·1 mm. During the distillation of the lower-boiling fractions (lævorotatory ethyl *p*-toluenesulphinate) the distillation flask was connected to a distillation "triangle" having taps of large bore, but for the higher-boiling fractions (lævorotatory β-octyl *p*-toluenesulphinate) even more open connexions had to be employed to ensure a higher vacuum in the distillation flask.

The first distillation revealed the presence of unchanged *l*-β-octanol (1 g.) and gave three further low-boiling fractions—II (6·8 g.), b. p. 74—80°; III (11·6 g.), b. p. 80—90°; and IV (1·2 g.), b. p.

90—100°—consisting largely of lævorotatory ethyl *p*-toluenesulphinate. These were refractionated and, after removal of a fraction (0·5 g.), b. p. 74—75°, fractions (*b*) (12·8 g.), b. p. 75—83°; (*c*) (4·0 g.), b. p. 83—85°; and (*d*) (1 g.), b. p. 85—90°, were obtained. Fraction (*b*) had $n_D^{25°}$ 1·5299, $\alpha_{5893}^{25°}$ — 2·81°, $\alpha_{5461}^{25°}$ — 3·46°, and $\alpha_{4359}^{25°}$ — 6·69° ($l = 0·5$). Its refractive index showed that it was impure lævorotatory ethyl *p*-toluenesulphinate, and therefore fractions (*b*), (*c*), and (*d*) were slowly refractionated; fractions (α) (3 g.), b. p. 72—74°, $n_D^{25°}$ 1·5295; (β) (4 g.), b. p. 74—75°, $n_D^{25°}$ 1·5309, $\alpha_{5461}^{25°}$ — 3·36° ($l = 0·5$); (γ) (5 g.), b. p. 75—76°, $n_D^{25°}$ 1·5309, $\alpha_{5461}^{25°}$ — 3·37° ($l = 0·5$); and (δ) (3 g.), b. p. 76—90°, were then obtained, leaving a residue (ε), 2 g.

Fractions (β) and (γ) were therefore lævorotatory ethyl *p*-toluenesulphinate.

The following experiments were made to prove that this lævorotatory ethyl *p*-toluenesulphinate unlike lævorotatory β-octyl *p*-toluenesulphinate, could not be separated by fractional distillation into fractions with different rotatory powers.

Four days after the determination of the physical constants recorded above, fraction (β) had $n_D^{25°}$ 1·5307 and $\alpha_{5461}^{25°}$ — 3·35° ($l = 0·5$), and fraction (γ) had $n_D^{25°}$ 1·5307 and $\alpha_{5461}^{25°}$ — 3·39° ($l = 0·5$). They were mixed and redistilled slowly in a very high vacuum. The first few drops of the distillate were neglected, the main fraction (6·7 g.), leaving a small dark residue, had b. p. 63°, $d_4^{25°}$ 1·114, $n_D^{25°}$ 1·5309, $n_{5461}^{25°}$ 1·5349, $n_{4359}^{25°}$ 1·5532, and $\alpha_{5893}^{25°}$ — 2·64°, $\alpha_{5461}^{25°}$ — 3·30°, $\alpha_{4359}^{25°}$ — 6·25° ($l = 0·5$). Three days later, it was redistilled in a similar vacuum and, again leaving a small, discoloured residue, was thus divided slowly into two portions of the same weight. They had $n_D^{25°}$ 1·5309, $\alpha_{5461}^{25°}$ — 3·27°, and $n_D^{25°}$ 1·5309, $\alpha_{5461}^{25°}$ — 3·22° ($l = 0·5$) respectively.

0·5984 of the portion which distilled first required 0·1817 of potassium hydroxide for complete hydrolysis (Theory, 0·1823).

In order to prove that the lævorotatory ethyl *p*-toluenesulphinate isolated did not consist of a mixture of (*a*) *l*-β-octanol, or of (*b*) lævorotatory β-octyl *p*-toluenesulphinate with inactive ethyl *p*-toluenesulphinate the following observations were made.

A portion of the ethyl *p*-toluenesulphinate from the same batch as that used in the preparation of the lævorotatory ester was inactive at 25° in a 200-mm. tube to light of λ 5461 and λ 4359.

0·3882 G. of *l*-β-octanol ($\alpha_D^{22°}$ — 8·06°; $l = 1·0$) was made up to 20 c.c. with this ethyl *p*-toluenesulphinate. The resulting solution had $d_4^{25°}$ 1·107, $n_D^{25°}$ 1·5281, and $\alpha_{5461}^{25°}$ — 0·58° ($l = 2·0$).

0·2314 G. of lævorotatory β-octyl *p*-toluenesulphinate ($n_D^{25°}$ 1·5053; $\alpha_{5461}^{25°}$ — 22·17°; $l = 0·5$) was added to 7·8602 g. of the ethyl *p*-toluene-

sulphinate. The resulting solution had $n_D^{25^\circ}$ 1·5297 and $\alpha_{5461}^{25^\circ}$ — 1·65°, $\alpha_{4359}^{25^\circ}$ —2·90° (l = 1·0).

Fifteen days after their separation and the determination of the rotatory powers recorded, the two portions of the optically active ethyl *p*-toluenesulphinate were mixed, and redistilled in a high vacuum; the mixture darkened rapidly and a black, tarry residue (0·5 g.) remained. The distillate (4·7 g.) had $n_D^{25^\circ}$ 1·5309 and $\alpha_{5461}^{25^\circ}$ — 0·04° (l = 1·0).

Oxidation of the lævorotatory ethyl p-*toluenesulphinate.* Twelve days after its isolation, fraction (δ) (p. 2578) was slowly redistilled in a high vacuum. The lower-boiling fraction was lævorotatory ethyl *p*-toluenesulphinate (1·85 g.) with $n_D^{25^\circ}$ 1·5308 and $\alpha_{5461}^{25^\circ}$ — 3·10° (l = 0·5). It was dissolved in acetone (30 c.c.), and a finely ground mixture of potassium permanganate (2 g.) and crystalline magnesium sulphate (1·6 g.) added in small quantities with agitation. The mixture was cooled and after 2 hours poured into water, and the manganese mud dissolved by the passage of sulphur dioxide. The heavy oil which separated, after being extracted, washed, and dried in ether, solidified (1·8 g.) in a vacuum; it had m. p. 34—35°, which was not depressed by admixture of the solid with ethyl *p*-toluenesulphonate.

The whole of the product made up to 20 c.c. with acetone gave a solution which was optically inactive in a 200 mm. tube.

Isolation of the lævorotatory β-*octyl* p-*toluenesulphinate formed during the preparation of the lævorotatory ethyl* p-*toluenesulphinate.* After the removal of fractions I, II, III, and IV during the distillation of the mixture of lævorotatory ethyl *p*-toluenesulphinate and lævorotatory β-octyl *p*-toluenesulphinate (p. 2573), the residual liquid in the distillation flask was distilled and gave fractions V (11·3 g.), b. p. 100—105°; VI (5 g.), b. p. 105—110°; and a dark residue VII (3 g.). By redistillation of the high-boiling residues left during the purification of the lævorotatory ethyl ester, lævorotatory β-octyl *p*-toluenesulphinate (1·3 g.), b. p. 100—105°/ < 0·1 mm., was obtained with $n_D^{25^\circ}$ 1·5053 and $\alpha_{5461}^{25^\circ}$ — 22·17° (l = 0·5). Fraction V above, without further purification, had $n_D^{25^\circ}$ 1·5054 and $\alpha_{5461}^{25^\circ}$ — 18·32° (l = 0·5). Fraction VI was lost, but on distillation of the residue VII a small quantity of lævorotatory β-octyl ester was obtained with $\alpha_{5461}^{25^\circ}$ — 8·55° (l = 0·25).

Thus it was shown that (*a*) the fractions of lævorotatory β-octyl *p*-toluenesulphinate obtained differed considerably in rotatory power, (*b*) the fraction which possessed the lowest rotatory power had $\alpha_{5461}^{25^\circ}$ — 34·20° (l = 1·0).

(b) *Lævorotatory* n-*Butyl* p-*Toluenesulphinate* (n-*Butyl* l + dl-p-*Toluenesulphinate.*—This was prepared in a similar manner to the

corresponding ethyl ester. The product of the interaction at 80°/16 mm., of *l*-β-octanol ($\alpha_D^{25°}$ — 8·04°; $l = 1·0$) (7·8 g.) and *n*-butyl *dl*-*p*-toluenesulphinate ($n_D^{25°}$ 1·5195), (25·7 g.), gave on distillation at a very low pressure a fraction (8·5 g.), b. p. 80—94°, $n_D^{25°}$ 1·5175, and $\alpha_{5461}^{25°}$ — 4·59° ($l = 0·5$). This was almost pure *n*-butyl *p*-toluenesulphinate. Four days after its isolation, it had $n_D^{25°}$ 1·5165 and $\alpha_{5461}^{25°}$ — 4·39° ($l = 0·5$). On redistillation, it darkened rapidly, but gave a distillate (6·9 g.), b. p. 80—84°, $n_D^{25°}$ 1·5189 and $\alpha_{5461}^{25°}$ — 2·24° ($l = 0·5$). Some racemisation had occurred, therefore, during the redistillation, and a further loss of rotatory power occurred during the last redistillation, when lævorotatory *n*-butyl *p*-toluenesulphinate (5·3 g.), b. p. 84°/< 0·1 mm., $d_4^{25°}$ 1·066, $n_D^{25°}$ 1·5195, and $\alpha_{5461}^{25°}$ — 1·73° ($l = 0·5$), was obtained.

(c) *Dextrorotatory Ethyl* p-*Toluenesulphinate* (*Ethyl* d + dl-p-*Toluenesulphinate*).—(i) *From* l-β-*octyl* l + dl-p-*toluenesulphinate*. The lævorotatory β-octyl *p*-toluenesulphinate used in this experiment was formed during the preparation of the lævorotatory ethyl *p*-toluenesulphinate, being made up of 1 g. with $\alpha_{5461}^{25°}$ — 22·17° ($l = 0·5$) and 11·3 g. with $\alpha_{5461}^{25°}$ — 18·32° ($l = 0·5$) (fraction V; p. 2579). The *l*-β-octyl ester dissolved in absolute ethyl alcohol (75 c.c.) containing potassium acetate (9 g.) was heated under reflux on a steam-bath for 28 hours, and the solution poured into water. The oil which separated, after being extracted and dried in ether, was distilled at less than 0·1 mm. Until fraction I, b. p. up to 40° (*l*-β-octanol), had been removed, a high vacuum could not be obtained. Fraction I (2 g.) was followed by fractions II (3·5 g.), b. p. 40—65°; III (2·2 g.), b.p. 70—94°; and IV (2·1 g.), b. p. 94—100°.

Fraction I, after two redistillations, had $\alpha_D^{22°}$ — 8·06° ($l = 1·0$), a value almost identical with that of the *l*-alcohol with which this series of experiments was commenced.

The succeeding fractions II, III, and IV were refractionated at a low pressure. The first fraction thus obtained, b. p. up to 65°, was carefully redistilled, and the first few drops of distillate were neglected. The main portion of the distillate (2 g.), b. p. 60—61°, had $n_D^{25°}$ 1·5309 and $\alpha_{5461}^{25°}$ + 0·46 ($l = 0·5$). 0·6072 required 0·1849 of potassium hydroxide for complete hydrolysis (Theory, 0·1850). It was therefore dextrorotatory ethyl *p*-toluenesulphinate.

The second fraction (2 g.), b. p. 65—100°, was obviously a mixture, but it was followed by the last fraction (2·5 g.), b. p. 100—106°, with $n_D^{25°}$ 1·5082 and $\alpha_{5461}^{25°}$ — 31·11° ($l = 0·5$). This was lævorotatory β-octyl *p*-toluenesulphinate, not of a high degree of purity, but possessing a much higher rotatory power than the *l*-sulphinate with

which this experiment was commenced. It is considered that it was produced during the separation of the mixture of dextrorotatory ethyl ester and *l*-β-octanol and did not arise owing to incomplete hydrolysis of the original lævorotatory β-octyl *p*-toluenesulphinate (compare the results of the experiment which follows).

(ii) *From* l-*menthyl* l + dl-p-*toluenesulphinate.* *l*-Menthyl *l* + *dl*-*p*-toluenesulphinate (m. p. 108—109°; $[\alpha]_{5461}^{17^\circ}$ − 239·9° in acetone, $c = 2{\cdot}609$, $l = 2{\cdot}0$) (27·2 g.) was heated under reflux for 60 hours with potassium acetate (18 g.) in absolute ethyl alcohol (250 c.c.). The reaction mixture was poured into water (1000 c.c.) and the crystals which separated from the oil were filtered off and washed with water. The oil which separated from the aqueous filtrate was isolated, washed and dried in ether, and fractionated at less than 0·1 mm., giving fractions I (4 g.), b. p. up to 60°; II (0·5 g.), III (4 g.), b. p. 65—72°; and leaving a black residue (about 1 g.) which solidified on cooling

Fraction I solidified to a white, crystalline solid, m. p. 42°, with $[\alpha]_{5893}$ − 48·8° in ethyl-alcoholic solution ($c = 5{\cdot}064$, $l = 2{\cdot}0$) and was therefore *l*-menthol. The original menthol from which the *p*-toluenesulphinate was prepared had $[\alpha]_{5893}$ − 49·46° under the same experimental conditions.

Fraction III had $n_D^{25^\circ}$ 1·5292 and $\alpha_{5461}^{25^\circ}$ + 7·37° ($l = 0{\cdot}5$). It was therefore impure dextrorotatory ethyl *p*-toluenesulphinate. After refractionation, it weighed 2·8 g., had b. p. 65°/ < 0·1 mm., $n_D^{25^\circ}$ 1·5306, and $\alpha_{5461}^{25^\circ}$ + 8·27° ($l = 0{\cdot}5$). A further redistillation completed its purification, dextrorotatory ethyl *p*-toluenesulphinate being obtained with $n_D^{25^\circ}$ 1·5309 and $\alpha_{5461}^{25^\circ}$ + 8·28° ($l = 0{\cdot}5$).

The crystals, *l*-menthyl *l* + *dl*-*p*-toluenesulphinate, which had been recovered by filtration of the diluted reaction mixture, were recrystallised from acetone. The first crop of crystals (8 g.), m. p. 108—109°, had $[\alpha]_{5461}^{17^\circ}$ − 241·9° in acetone ($c = 2{\cdot}751$, $l = 2{\cdot}0$). On dilution of the mother-liquor with water, a second crop of crystals (4 g.) was obtained, m. p. 107—108°, with $[\alpha]_{5461}^{17^\circ}$ − 237·8 in acetone ($c = 2{\cdot}670$, $l = 2{\cdot}0$). It cannot be assumed, therefore, that any preferential alcoholysis of the original *l*-menthyl *l* + *dl*-*p*-toluenesulphinate occurred.

(iii) *From* dl-p-*toluenesulphinyl chloride after it had been treated with half of its equivalent quantity of* l-β-*octanol.* To a solution of *dl*-*p*-toluenesulphinyl chloride (34·4 g.; 2 mols.) in light petroleum (75 c.c.) cooled in a freezing mixture, a solution of *l*-β-octanol ($\alpha_D^{26^\circ}$ − 8·04°; $l = 1{\cdot}0$) (13 g.; 1 mol.) in pyridine (7·9 g.; 1 mol.) was added during 2½ hours with agitation. At the end of ½ hour a solution of ethyl alcohol (9 g.) in pyridine (10 g.) was added, and the mixture, having stood for 12 hours, was washed three times with

water, twice with dilute hydrochloric acid, and twice again with water, and then dried over potassium carbonate. The solvent was removed, and the residual oil fractionated at less than 0·1 mm. It gave fractions I (11·7 g.), b. p. up to 84°, $n_D^{25°}$ 1·5078, $\alpha_{5461}^{25°}$ — 1·74° (l = 1·0); II (3·7 g.), b. p. 84—90°, $n_D^{25°}$ 1·5233, $\alpha_{5461}^{25°}$ + 1·83° (l = 0·5); III (11·5 g.), b. p. 90—100°, $n_D^{25°}$ 1·5022, $\alpha_{5461}^{25°}$ — 15·08° (l = 0·5); IV (6·5 g.), b. p. 110—112°, $n_D^{25°}$ 1·5044, $\alpha_{5461}^{25°}$ — 13·14° (l = 0·5), and left a black, tarry residue (3·5 g.). Fraction I was refractionated and gave fractions (*a*) (5·5 g.), $n_D^{25°}$ 1·5037, $\alpha_{5461}^{25°}$ — 3·52° (l = 0·5); (*b*) (1·5 g.), $n_D^{25°}$ 1·5202; and (*c*) (2·8 g.), $n_D^{25°}$ 1·5269, $\alpha_{5461}^{25°}$ + 1·3° (l = 0·5).

It appeared probable that fractions II, (*b*), and (*c*) were impure dextrorotatory ethyl *p*-toluenesulphinate. Seven days after they had been isolated, they were mixed and fractionated at a very low pressure. The mixture darkened rapidly, but gave fractions (α) (1 g.), $n_D^{25°}$ 1·5302, $\alpha_{5461}^{25°}$ — 0·05° (l = 0·25), and (β) (3·2 g.), $n_D^{25°}$ 1·5299, $\alpha_{5461}^{25°}$ — 0·13° (l = 0·5), leaving a large, non-volatile residue.

These results are consistent with the view that fractions II, (*b*), and (*c*) were mixtures of dextrorotatory ethyl *p*-toluenesulphinate and lævorotatory β-octyl *p*-toluenesulphinate, and that during their last distillation the dextrorotatory ethyl ester racemised, giving fractions (α) and (β), which were presumably inactive ethyl *p*-toluenesulphinate contaminated with traces of the lævorotatory β-octyl ester.

That some preferential reaction on the part of the *dl*-*p*-toluenesulphonyl chloride took place is probable, since the lævorotatory β-octyl *p*-toluenesulphinate produced, fractions III and IV, combined and then redistilled, had $n_D^{25°}$ 1·5028 and $\alpha_{5461}^{25°}$ — 15·21° (l = 0·5), a value approximating to the rotatory power of the β-octyl ester obtained when *l*-β-octanol (1 mol.) preferentially reacts with ethyl *dl*-*p*-toluenesulphinate (2 mols.).

Two attempts were made to repeat this experiment, but in each case the pure ethyl *p*-toluenesulphinate finally isolated was inactive, although the distillation was not interrupted and was unattended by excessive charring of the fractions on redistillation. Indeed, the rotatory powers of the various fractions obtained gave no indication of any preferential reaction of the *dl*-*p*-toluenesulphonyl chloride with the *l*-β-octanol. Especially was this true of the lævorotatory β-octyl *p*-toluenesulphinate isolated (completely) in one of the experiments, for its rotatory power was $\alpha_{5461}^{25°}$ — 24·5° (l = 1·0), approximating to that of the β-octyl ester obtained by the interaction of *l*-β-octanol (1 mol.) and ethyl *dl*-*p*-toluenesulphinate (1 mol.).

(d) *Lævorotatory* p-*Toluenesulphinanilide*.—(i) *From* dl-p-*toluene*-

sulphinyl chloride after it had been treated with half its equivalent quantity of l-β-*octanol.* *p*-Toluenesulphinyl chloride (34·4 g.; 2 mols.) in ether (150 c.c.) was treated as described in the preceding experiment with a solution of *l*-β-octanol ($\alpha_D^{25°}$ − 8·04°; l = 1·0) (13 g.; 1 mol.) in pyridine (7·9 g.); to the resulting mixture, aniline (19 g.) was added. After 12 hours, the crystals formed were filtered off, washed with water (to dissolve the hydrochlorides of pyridine and aniline), pressed on a porous plate, and recrystallised from aqueous ethyl alcohol. *p*-Toluenesulphinanilide was thus obtained in nacreous plates, m. p. 134° (Braun and Kaiser, *loc. cit.*, give m. p. 138°), $[\alpha]_{5461}^{17°}$ − 1·1° in chloroform (c = 5·000, l = 2·0), and $[\alpha]_{5461}^{17°}$ − 0·65° in pyridine (c = 4·669, l = 2·0) (Found: N, 6·2%. Calc., N, 6·1).

(ii) *From* dl-p-*toluenesulphinyl chloride after it had been treated with half its equivalent quantity of* l-*menthol.* To *p*-toluenesulphinyl chloride (17·2 g.; 2 mols.) a solution of *l*-menthol (7·8 g.; 1 mol.) in pyridine (11·7 g.; 2 mols.) was slowly added during 3 hours. After the addition of aniline (10 g.), the mixture was kept for 12 hours, water was then added, the aqueous mixture filtered, and the crystals thus isolated (a mixture of lævorotatory menthyl *p*-toluenesulphinate and *p*-toluenesulphinanilide), after they had been washed with water, dilute hydrochloric acid and then again with water, were treated with ether (50 c.c.) to dissolve the lævorotatory menthyl *p*-toluenesulphinate. The ethereal extract was filtered, and the almost insoluble *p*-toluenesulphinanilide obtained, having been washed with a further 10 c.c. of ether, was dried, and recrystallised from benzene; it then had $[\alpha]_{5461}^{25°}$ − 1·29° in chloroform (c = 5·400, l = 2·0).

Conversion of Lævorotatory Ethyl p-*Toluenesulphinate* (*Ethyl* l + dl-p-*Toluenesulphinate*) *into Dextrorotatory* n-*Butyl* p-*Toluenesulphinate* (n-*Butyl* d + dl-p-*Toluenesulphinate*).

Lævorotatory ethyl *p*-toluenesulphinate ($\alpha_{5461}^{25°}$ − 2·91°; l = 0·5) (14·5 g.), prepared as previously described, was warmed gently under reflux with *n*-butyl alcohol (5·8 g.) for 18 hours, the apparatus being evacuated to 15 mm. On fractional distillation of the product at less than 0·1 mm., two fractions were obtained: I (10·7 g.), b. p. 85—86°, $n_D^{25°}$ 1·5259, $\alpha_{5461}^{25°}$ − 0·39° (l = 1·0); and II (1·9 g.), b. p. 85—86°, $n_D^{25°}$ 1·5159, and $\alpha_{5461}^{25°}$ + 0·08° (l = 0·25).

Fraction II was pure *n*-butyl *p*-toluenesulphinate. Fraction I was a mixture of the ethyl and *n*-butyl esters and was refractionated twice, giving finally fractions (*a*), 3·0 g., b. p. 66—72°, $n_D^{25°}$ 1·5296, $\alpha_{5461}^{25°}$ − 0·33° (l = 0·5); (*b*), 1·8 g., b. p. 72—74°, $n_D^{25°}$ 1·5286, $\alpha_{5461}^{25°}$ − 0·18° (l = 0·5), and (*c*), 1·7 g., $n_D^{25°}$ 1·5238, − 0·03°

($l = 0{\cdot}25$). Fraction (*c*) was redistilled and gave 1 g., $n_D^{25°}$ 1·5207. This was therefore almost pure *n*-butyl *p*-toluenesulphinate. It had $\alpha_{5461}^{25°} + 0{\cdot}05$ ($l = 0{\cdot}25$).

Reactions of the p-*Toluenesulphonic Esters of* l-*Menthol and of* l-β-*Octanol.*

Conversion of l-*Menthol into* d-neo*Menthol.*—l-*Menthyl* p-*toluenesulphonate* (compare Hilditch, *loc. cit.*) was prepared as required by the addition of finely ground *p*-toluenesulphonyl chloride (1 mol.) to an ice-cold solution of *l*-menthol (1 mol.) in pyridine (1·25 mols.). The mixture was shaken until homogeneous and after 12 hours set to a hard, crystalline mass, which was crushed, extracted with water, dried, and recrystallised from ethyl alcohol. It then had m. p. 96° and $[\alpha]_{5893} - 70{\cdot}16°$ in chloroform ($c = 2{\cdot}620$, $l = 2{\cdot}0$).

Reaction between l-*Menthyl* p-*Toluenesulphonate and Glacial Acetic Acid.*—A solution of the *l*-sulphonate (150 g.) in the acid (200 c.c.) was warmed gently on a water-bath for 12 hours. The product was neutralised with a dilute solution of potassium carbonate and the oil which separated was extracted with ether. The mixture of menthene and menthyl acetates obtained, after removal of the ether from this ethereal extract, was refluxed with alcoholic sodium hydroxide, and the liberated menthols were isolated in a current of steam. They were heated with phthalic anhydride (80 g.) at 110° for 15 hours, and the mixture of menthene and menthyl hydrogen phthalates thus obtained was poured into a dilute sodium carbonate solution. The menthene was extracted from this solution with ether, and was isolated from the dried ethereal extract as a colourless oil, b. p. 64—65°/18 mm., $d_4^{23°}$ 0·8185, $n_D^{25°}$ 1·4540, and $\alpha_D^{24°} + 16{\cdot}58°$ ($l = 1{\cdot}0$). (Henderson and Boyd, J., 1911, **99**, 2159, give $d_{20°}^{20°}$ 0·8180, n_D 1·4536, for Δ^3-menthene. The menthene obtained, therefore, was in all probability that hydrocarbon.)

The hydrogen phthalic esters were recovered from the acidified sodium carbonate solution and had $[\alpha]_D - 62{\cdot}6°$ ($c = 5{\cdot}107$, $l = 2{\cdot}0$) in chloroform solution. Pure *l*-menthyl hydrogen phthalate under the same experimental conditions has $[\alpha]_D - 91{\cdot}40°$ (Pickard and Littlebury, *loc. cit.*).

It was presumed that the mixture of hydrogen phthalic esters obtained was a mixture of those of *l*-menthol and *d-neo*menthol. A partial separation was effected by precipitating the bulk of the *l*-menthyl hydrogen phthalate as its magnesium salt by the addition of magnesium sulphate solution to a neutral solution of the sodium salts of the esters. The magnesium salt obtained was filtered off, recrystallised from aqueous ethyl alcohol, and reconverted into the hydrogen phthalic ester, which was further purified by recrystallis-

ation from acetic acid. When dry, the ester thus obtained had m. p. 110—112° and $[\alpha]_D$ — 91·90° in chloroform ($c = 5{\cdot}362$, $l = 2{\cdot}0$). It was therefore pure *l*-menthyl hydrogen phthalate.

The remaining phthalic esters were precipitated as zinc salts by addition of zinc chloride to the filtrate from the magnesium *l*-menthyl phthalate. The zinc salts were dissolved in acetic acid and reprecipitated, by the addition of water, as hydrogen phthalic esters, which when dry had m. p. 139—142° and $[\alpha]_D$ + 14·60° in chloroform ($c = 2{\cdot}532$, $l = 2{\cdot}0$).

It was considered impossible to purify satisfactorily the small quantity of *d-neo*menthyl hydrogen phthalate obtained, and therefore the following steps were taken to prove that only the hydrogen phthalates of *l*-menthol and of *d-neo*menthol were present in the original mixture.

With the exception of the pure *l*-menthyl hydrogen phthalate which had been isolated, the whole of the phthalic esters originally obtained were recovered, hydrolysed by refluxing them with an alcoholic solution of potassium hydroxide, and the liberated menthols were isolated in a current of steam. When redistilled, they had b. p. 103—107°/17 mm., $n_D^{17\cdot5°}$ 1·4603, and $\alpha_D^{17°}$ — 28·94° ($l = 1{\cdot}0$) (Pickard and Littlebury, *loc. cit.*, p. 122, record $n_D^{20°}$ 1·4603 and $[\alpha]_D$ + 19·69° for *d-neo*menthol).

The mixture of menthols thus obtained was oxidised by the method of Beckmann (*Annalen*, 1889, **250**, 325). The menthone produced had b. p. 89—91°/16 mm., $\alpha_D^{20°}$ — 5·44° ($l = 0{\cdot}25$), $d_4^{20°}$ 0·869, whence $[\alpha]_D^{20°}$ — 24·28° (Pickard and Littlebury, *loc. cit.*, p. 124, state that *l*-menthol and *d-neo*menthol alone when oxidised by the above method give *l*-menthone of rotatory power between $[\alpha]_D$ — 23·3° and $[\alpha]_D$ — 29·10°).

By shaking the *l*-menthone obtained with an aqueous methyl-alcoholic solution of equivalent proportions of semicarbazide hydrochloride and potassium acetate, its semicarbazone was produced which, after drying, had m. p. 186—188° (Pickard and Littlebury, *loc. cit.*, give m. p. 189° for the semicarbazone of pure *l*-menthone).

It was thus proved that only two menthols were produced, giving hydrogen phthalic esters of opposite sign of rotatory power, and since they both gave *l*-methone on oxidation they were *l*-menthol and *d-neo*menthol, respectively.

Reaction between l-*Menthyl* p-*Toluenesulphonate and Ammonium Acetate.*—A mixture of the *l*-ester (15·5 g.) and ammonium acetate (38·5 g.) was heated with occasional shaking for 96 hours at 110°, and then distilled with steam. The product isolated from the distillate with ether, on distillation, gave fraction I (3 g.), b. p. 60—64°/17 mm., which was a menthene, and fraction II (1 g.),

b. p. 105—107°/17 mm., which was *d-neo*menthol (containing some *l*-menthol) with $\alpha_D^{17^\circ} + 2{\cdot}5^\circ$ ($l = 0{\cdot}25$). It readily gave a phenylcarbamate which, after recrystallisation from methyl alcohol, had m. p. 104°.

Interconversion of the Enantiomorphously related β-*Octanols.* l-β-*Octyl* p-*Toluenesulphonate.*—Lævorotatory β-octyl *p*-toluenesulphinate ($\alpha_D^{16^\circ} - 9{\cdot}64^\circ$; $l = 1{\cdot}0$) (16 g., prepared by the interaction of *l*-β-octanol, $\alpha_D^{18^\circ} - 8{\cdot}04^\circ$ [$l = 1{\cdot}0$] and *p*-toluenesulphinyl chloride in presence of pyridine) was dissolved in acetone (120 c.c.), and a solution of magnesium sulphate (10 g.) in water (50 c.c.) added. The mixture was vigorously stirred during the addition of finely divided potassium permanganate (10 g.). The solution, now permanently coloured, was diluted with water, and sulphur dioxide passed into the solution until the manganese mud had just dissolved. It was then cooled, extracted with ether, the ethereal extract dried over potassium carbonate, and the ether removed by distillation. *l*-β-Octyl *p*-toluenesulphonate (14 g.) was thus obtained as a colourless oil which showed no tendency to crystallise even when cooled in liquid air. It had $\alpha_D^{19^\circ} - 6{\cdot}78^\circ$, and decomposed rapidly when heated at 110°/0·1 mm.

Reaction between l-β-*Octyl* p-*Toluenesulphonate and Potassium Acetate in Ethyl-alcoholic Solution.*—The *l*-ester (14 g.; $\alpha_D^{19^\circ} - 6{\cdot}78^\circ$) was added to absolute ethyl alcohol (75 c.c.) containing freshly fused potassium acetate (9·8 g.). After 17 hours' heating under reflux, the reaction mixture was poured into water and the oil which separated isolated with ether in the usual manner. On distillation, a small fraction was obtained below 82°/17 mm. which was unsaturated, and after the main fraction (5 g.), b. p. 82—92°/17 mm., had distilled, only a small, gummy residue remained. After three refractionations of the main fraction, *d*-β-octyl acetate (1·5 g.) was obtained the rotatory power of which was unaltered by subsequent redistillation. It had $d_4^{17^\circ}$ 0·8619, $n_D^{17^\circ}$ 1·4168, and $\alpha_D^{17^\circ} - 5{\cdot}64^\circ$ ($l = 1{\cdot}0$) (compare Part V, *loc. cit.*, and p. 2565 of this paper).

Reaction between d-β-*Octyl* p-*Toluenesulphonate and Potassium Benzoate in Ethyl-alcoholic Solution.*—The *d*-ester ($\alpha_D^{26{\cdot}5^\circ} + 7{\cdot}30^\circ$; $l = 1{\cdot}0$) (25 g.; obtained by the oxidation of a *p*-toluenesulphinate of *d*-β-octanol, with $\alpha_D^{19^\circ} + 18{\cdot}18^\circ$ [$l = 1{\cdot}0$]), and potassium benzoate (28 g.) in absolute ethyl alcohol (123 c.c.) were heated under reflux for 12 hours, and the products isolated as previously described. On distillation, two fractions were obtained: I (6 g.), b. p. 74—83°/19 mm.; II (5 g.), b. p. 83—170°/19 mm.

Fraction I was crude *l*-β-octyl ethyl ether. It was heated with phthalic anhydride (10 g.) at 110° for 15 hours, and the resulting mixture poured into a dilute solution of sodium carbonate. When all

the solid matter had dissolved, this solution was extracted with ether, and from the dried extract the *l*-β-octyl ethyl ether (now free from traces of β-octanol) was regained and fractionated until further redistillation left its rotatory power unchanged. It then had b. p. 73—74°/17 mm., $d_{4^\circ}^{20^\circ}$ 0·7836, $n_{5893}^{25^\circ}$ 1·4081, $n_{5496}^{24\cdot5^\circ}$ 1·4099, and $\alpha_{\mathrm{D}}^{23^\circ}$ — 14·08°, $\alpha_{5461}^{23^\circ}$ — 16·64° and $\alpha_{4359}^{23^\circ}$ — 26·92° ($l = 1{\cdot}0$).

(These values are somewhat higher than those given in Part XIV, J., 1923, **123**, 14, where the *l*-β-octyl ether described was prepared directly from *l*-β-octanol, and should therefore be compared with the values obtained for the *d*-β-octyl ethyl ether prepared as described below.)

Fraction II was *l*-β-octyl benzoate. It was refractionated four times; its rotatory power then could not be changed by further redistillation. (The small increases in its rotatory power produced during the preliminary fractionations were attributable to purification; no evidence of the separation of the ester into two forms with different rotatory powers could be obtained.) The *l*-β-octyl benzoate obtained had b. p. 168°/18 mm., $d_{4^\circ}^{21^\circ}$ 0·9679, $n_{\mathrm{D}}^{21^\circ}$ 1·4864, and $\alpha_{\mathrm{D}}^{23^\circ}$ — 28·70° (compare Part XII, J., 1915, **107**, 121). By hydrolysis with alcoholic sodium hydroxide, *l*-β-octanol was obtained with $\alpha_{\mathrm{D}}^{23^\circ}$ — 6·96° ($l = 1{\cdot}0$).

d-β-*Octyl Ethyl Ether.*—*d*-β-Octanol ($\alpha_{\mathrm{D}}^{16^\circ}$ — 8·10°; $l = 1{\cdot}0$) (7 g.) was added to powdered potassium (1·9 g.) in ether (100 c.c.). After dissolution of the potassium, ethyl *p*-toluenesulphonate (15 g.) was added in small quantities, and after 12 hours, the mixture was refluxed for 3 hours. The reaction mixture was then distilled in steam, and the crude *d*-β-octyl ethyl ether isolated in the usual manner and heated with phthalic anhydride (15 g.) as previously described. The purified *d*-β-octyl ethyl ether was redistilled until of constant rotatory power, when it had b. p. 73—74°/17 mm., $d_{4^\circ}^{20^\circ}$ 0·7838, $n_{\mathrm{D}}^{21^\circ}$ 1·4095, $n_{5461}^{21^\circ}$ 1·4105 and $\alpha_{5893}^{21\cdot5^\circ}$ + 15·38, $\alpha_{5461}^{21\cdot5^\circ}$ + 18·08, $\alpha_{4359}^{21\cdot5^\circ}$ + 33·36° ($l = 1{\cdot}0$).

It is possible that this *d*-β-octyl ethyl ether thus prepared was optically impure, since the use of ethyl *p*-toluenesulphonate as an alkylating agent may lead to loss of rotatory power (Part XVII, *loc. cit.*).

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CCCLV.—*The Relation between Chemical Constitution and Pungency in Acid Amides.*

By EDWARD CHARLES SNELL JONES and FRANK LEE PYMAN.

THE constitution of piperine has long been known, and the discoveries of Nelson (*J. Amer. Chem. Soc.*, 1919, **41**, 1115) that capsaicin is a decenovanillylamide and of Asahina and Asano (*J. Pharm. Soc. Japan*, 1922, 85) that the reduction product of spilanthol, the pungent principle of para-cress, is *n*-deco*iso*butylamide have aroused considerable interest in the connexion between chemical constitution and pungency in acid amides.

Nelson (*J. Amer. Chem. Soc.*, 1919, **41**, 2121) prepared the vanillylamides of the normal fatty acids up to dodecoic, and found that the pungency became pronounced with the *n*-hexo-derivative, increased up to the *n*-nono-derivative, and then diminished. He prepared also a few vanillylamides of aromatic and unsaturated aliphatic acids, of which the most important was Δ^{ω}-undecenovanillylamide. His estimate of the relative pungency of his more active vanillylamides was *n*-hexo 5, *n*-hepto 25, *n*-octo 75, *n*-nono 100, *n*-deco 50, *n*-undeco 25, *n*-dodeco 25, and Δ^{ω}-undeceno 25, as compared with capsaicin 100.

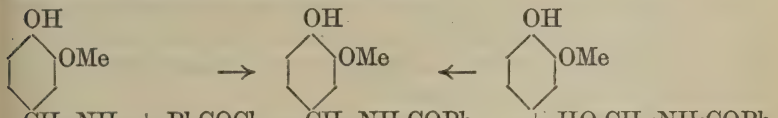
Ott and Zimmermann (*Annalen*, 1921, **425**, 314) prepared several vanillylamides and concluded from the fact that they found the vanillylamides of a number of unsaturated acids and especially oleovanillylamide to be very pungent whilst stearovanillylamide was tasteless, that pungency is associated with unsaturation in the acyl group. Their view, however, has been shown to be incorrect by Nelson and Dawson (*J. Amer. Chem. Soc.*, 1923, **45**, 2179), who find that dihydrocapsaicin (η-methylnonovanillylamide) is just as pungent as capsaicin itself, which they showed to have the constitution of η-methyl-Δ^{ϵ}-nonenovanillylamide.

Nelson did not study the effect of varying the basic part of the molecule except that both he and Lapworth and Royle (J., 1919, **115**, 1109) state that the methyl ether of capsaicin is far less pungent than capsaicin. Ott and Zimmermann, however, prepared and noted the pungency of the Δ^{ω}-undeceno-derivatives of benzylamide (tasteless) and its 4-methoxy- (tasteless) and 2- and 4-hydroxy-derivatives (fairly pungent, $4>2$).

Staudinger and Schneider (*Ber.*, 1923, **56**, 699) and Staudinger and Müller (*ibid.*, p. 711) studied the pungency of a series of piperidides. They found the piperidides of aliphatic or purely aromatic acids to be only feebly pungent, whilst, in the pungency of the piperidides of the ω-phenyl normal saturated fatty acids, a distinct

maximum effect was found, the δ-phenyl-*n*-valero-derivative being very pungent whilst γ-phenyl-*n*-butyro- and ε-phenyl-*n*-hexo-piperidides were only slightly pungent. The three δ-phenylpenteno-piperidides also were found to be very pungent, whilst γ-phenyl-Δ^{β}-*iso*crotonopiperidide was only feebly pungent. They therefore associated the pungency of piperidides with the skeleton rather than with the state of saturation of the acyl residue.

The present work was started with the object of preparing substances exceeding capsaicin in pungency, and a number of acylbenzylamides have been made. The method mainly employed was that of Nelson, namely, the action of acyl chlorides upon benzylamines, but a number of vanillylamides have been prepared by a method due to Einhorn (*Annalen*, 1905, **343**, 207), namely, the condensation of the *N*-methylol derivatives of acid amides with guaiacol. Einhorn did not determine the orientation of his condensation products, but it is now shown that substitution took place in the para-position with respect to the hydroxy-group, since benzo-, chloroaceto-, and Δ^{ω}-undeceno-vanillylamides have been made both by the action of the acid chloride upon vanillylamine and by the condensation of the *N*-methylol derivative of the acid amide with guaiacol. The formation of benzovanillylamide by the two methods is formulated below:



After this result had been obtained, Bradner and Sherrill (U.S. Pat. 1503631 of 1924) recorded the formation of a pungent compound of undetermined constitution by the condensation of guaiacol with *N*-methylol-Δ^{ω}-undecenoamide.

In the course of the present work, we have varied both the acyl and the amido-residue. In varying the first, we were interested to find out how far the predominance of *n*-nonovanillylamide amongst Nelson's synthetic compounds was due to the length of the acyl residue and how far to its mass. From this point of view, we have prepared and examined the pungency of the vanillylamides of (1) a branched-chain nonoic acid, (2) a series of ω-phenyl saturated fatty acids, and (3) a number of halogeno-acetic acids. The results were as follows: (1) α-iso*Propyl*-n-*hexovanillylamide* has only about 5% of the pungency of *n*-nonovanillylamide. (2) Whilst benzovanillylamide is faintly pungent and *phenylacetovanillylamide* non-pungent, β-*phenylpropiovanillylamide* has some 40% of the pungency of *n*-nonovanillylamide and γ-*phenyl*-n-*butyro*- and

δ-*phenyl*-n-*valero-vanillylamides* are slightly more pungent. The latter results may be contrasted with Staudinger's experiences with the piperidides, where a distinct maximum effect was experienced with the δ-phenyl-*n*-valero-derivative. It may be added here that the pungency of cinnamovanillylamide is trivial compared with that of its dihydro-derivative, β-phenylpropiovanillylamide, and this result supports the opinion of Nelson and controverts that of Ott and Zimmermann as regards the effect of unsaturation on pungency.

(3) The pungency of the *mono-*, *di-*, and *tri-chloroacetovanillylamides* and of *bromo-* and *iodo-acetovanillylamides* was only slight and of the same order. It therefore appears that the shape rather than the weight of the side-chain is the important factor in the matter of pungency.

Experiments in which the acyl group—*n*-nonoyl or undecenoyl—remained constant, whilst the amido-residue was varied, largely bore out the conclusions of Ott and Zimmermann. Where no phenolic hydroxyl was present in the molecule, as in n-*nono*-3 : 4-*methylenedioxybenzylamide* and n-*nono*-4-*methoxybenzylamide*, no pungency was observed, whilst n-*nono*-4-*hydroxybenzylamide* had about 10% and Δ^{ω}-undeceno-4-hydroxybenzylamide about 30% of the pungency of *n*-nonovanillylamide. The introduction of a further hydroxy-group into the meta-positions in these compounds increases the pungency still further, for the n-*nono*- and Δ^{ω}-*undeceno*-3 : 4-*dihydroxybenzylamides* had respectively 25 and 50% of the pungency of *n*-nonovanillylamide.

The relative pungency of these compounds was determined by Pearson's method (*Pharm. J.*, 1919, **103**, 78), that is, by dilution of aqueous-alcoholic solutions with water until pungency was barely perceptible when a few drops of the solution were tasted. The results are to be regarded as only approximately quantitative, because of the variation in the kind of taste of the compounds as well as the difficulty of comparing the intensities of tastes of the same kind. Some of these compounds have a purely pungent taste, whilst the taste of others is a blend of flavour and pungency, and, further, the pungency itself varies from a crisp and transient sting to a dull, persistent, numbing burn. Thus at a dilution of 1 in 500,000 *n*-nonovanillylamide causes an immediate crisp sting, free from flavour, the effects of which last for 2 minutes, Δ^{ω}-undeceno-vanillylamide produces a dull numbing burn which takes two or three seconds to develop and persists for 8 minutes, and has also an inky flavour, whilst capsaicin rapidly produces a vigorous burn lasting 6 minutes, and has also a flavour. On further dilutions to 1 in 5,000,000, the pungency of *n*-nonovanillylamide is barely

perceptible, whilst that of Δ^{ω}-undecenovanillylamide and capsaicin is still faint, and therefore we regard these two compounds as rather more pungent than *n*-nonovanillylamide, whereas Nelson, who also comments on the varying character of the pungencies of these compounds, regards *n*-nonovanillylamide as being four times as pungent as Δ^{ω}-undecenovanillylamide.

Experimental.

Preparation of Acylbenzylamides by Nelson's Method.—The following general method was employed for the preparation of acylbenzylamides other than the halogeno-acetovanillylamides. The acid chloride (1 mol.) was added gradually to a solution or suspension of the dry amine (2 mols.) in sodium-dried ether, and the mixture was kept for 1 or 2 days with occasional shaking. The reaction product was extracted with 3% hydrochloric acid to remove the unchanged amine, and in the case of the sparingly soluble benzo-, phenylaceto-, cinnamo-, and αβ-dichloro-β-phenylpropio-vanillylamides the bulk of the acid amide was filtered off at this point. In the other cases, the ethereal solution was extracted with aqueous sodium carbonate to decompose unchanged acid chloride and to remove the acid; it then left, on distillation, the crude acid amide. Where the product contained a free phenolic hydroxyl group, however, it proved to be advantageous to extract it from the ethereal solution with aqueous sodium hydroxide, and after acidifying this solution to collect it by means of ether, thereby eliminating or hydrolysing any *O*-acyl derivative present. The products were finally crystallised from the solvents mentioned in the table on page 2593, and obtained in the yields stated there. We attribute the higher melting points of our preparations of nono- and undeceno-vanillylamides as compared with Nelson's, in part to the extraction with sodium hydroxide mentioned above, and in part to the fact that we dried vanillylamine in a vacuum over sulphuric acid, whilst Nelson dried it at 110°. This difference in procedure is important, for vanillylamine suffers decomposition when heated with water at 100°, as Nelson has pointed out.

In the case of chloroacetovanillylamide, where the above method could not be employed owing to the solubility of this substance in aqueous vanillylamine hydrochloride, and its sparing solubility in solvents immiscible with water, the following procedure was adopted. To anhydrous vanillylamine (20 g.) suspended in dry ether chloroacetyl chloride (7·4 g.) was added drop by drop. After the vigorous reaction was complete the ether was removed by distillation, and the acid amide collected by prolonged extraction with hot chloroform. Dichloro- and monobromo-acetovanillylamides were isolated

similarly, but whilst dichloroacetyl chloride reacted immediately and vigorously with vanillylamine, the reaction between bromoacetyl bromide and the amine was very sluggish, and gave only a 28% yield after keeping for 3 weeks. Attempts to improve the yield by heating bromoacetyl bromide and vanillylamine with benzene, xylene, or ether in the presence of pyridine were unsuccessful.

Trichloroacetovanillylamide was obtained by adding trichloroacetic anhydride (20·2 g.) to anhydrous vanillylamine (20 g.) suspended in dry ether, regulating the reaction by cooling, removing vanillylamine trichloroacetate by filtration, and washing the ethereal solution with aqueous sodium carbonate, when it remained after removing the solvent.

Iodoacetovanillylamide was prepared in theoretical yield by boiling chloroacetovanillylamide with sodium iodide in acetone solution for ½ hour. Dichloroacetovanillylamide did not react with sodium iodide under these conditions, but the solution deposited sodium chloride after several hours at 120°. No sodium chloride was deposited after heating trichloroacetovanillylamide with sodium iodide in acetone solution for 10 hours at 150°.

Properties of the Acylbenzylamides. — The acylbenzylamides described below are colourless, except iodoaceto- and β-*p*-nitrophenylpropio-vanillylamides, which are straw-coloured, and nono- and undeceno-3 : 4-dihydroxybenzylamides, which could not be obtained free from brown colour. The monohalogenoacetovanillylamides are moderately easily soluble in hot water, the remainder being almost insoluble.

The vanillylamides of benzoic, phenylacetic, cinnamic, and the halogenated acids (except trichloroacetic) are sparingly soluble in ether, and generally less soluble in the usual organic solvents than the remaining acid amides.

Particulars of the individual compounds are given in the tables on pages 2593–5.

Substituted Benzylamines.—These are prepared usually by the reduction of substituted benzaldoximes by means of sodium amalgam and glacial acetic acid in alcohol at about 60°.

Nelson (*loc. cit.*) prepared vanillylamine from vanillinoxime in this way in an average yield of 65%, but Ott and Zimmermann (*loc. cit.*) failed to confirm this yield even approximately. We find that reduction by this means is best conducted below 30°, when good yields are obtained, the yield of vanillylamine from vanillinoxime being 75—80%, that of 3 : 4-methylenedioxybenzylamine from piperonaldoxime 92%, and that of anisylamine from anisaldoxime 80%.

Acylbenzylamides.

Substance.	Yield in per cent. of theory.	Crystalline form and solvent employed for crystallisation.	M. p. (corr.).	Analysis. Per cent. C.	Per cent. H.	Formula.	Required. Per cent. C.	Per cent. H.	Pungency.
n-Nonovanillylamide	86	Microscopic needles* from ethyl acetate	57—59°†	69·4	9·3	$C_{17}H_{27}O_3N$	69·6	9·3	100
α-*iso*Propyl-*n*-hexovanillylamide	80	Fine needles from ether	124—125	69·6	9·3	$C_{17}H_{27}O_3N$	69·6	9·3	5
Δ^{ω}-Undecenovanillylamide	89	Nodules of microscopic needles from ether	58—60 ‡	71·3	9·1	$C_{19}H_{29}O_3N$	71·4	9·2	>100
Benzovanillylamide	90	Prisms from alcohol	144—145 §	69·8	5·9	$C_{15}H_{15}O_3N$	70·0	5·9	0·5
Phenylacetovanillylamide	80	Needles from alcohol	112	70·7	6·4	$C_{16}H_{17}O_3N$	70·8	6·3	0‖
β-Phenylpropiovanillylamide	88	Needles from ethyl acetate *	80—83	71·4	6·8	$C_{17}H_{19}O_3N$	71·5	6·7	40
γ-Phenyl-*n*-butyrovanillylamide	85	Leaflets from ether	93—95	72·1	7·1	$C_{18}H_{21}O_3N$	72·2	7·1	>40
δ-Phenyl-*n*-valerovanillylamide	85	Clusters of needles from a mixture of ether and light petroleum	67	72·8	7·5	$C_{19}H_{23}O_3N$	72·8	7·4	>40

* On cooling in freezing mixture.
† Nelson, 47—52°.
‡ Nelson, 54—56°; Ott and Zimmermann, 40°.
§ Einhorn, 148°; Nelson, 140—442°.
‖ 0 means pungency not perceptible 1 in 1000.

Substance.	Yield in per cent. of theory.	Crystalline form and solvent employed for crystallisation.	M. p. (corr.).	Analysis. Per cent. C.	Per cent. H.	Formula.	Required. Per cent. C.	Per cent. H.	Pungency.
β-p-Nitrophenylpropiovanillylamide	80	Dense prisms from alcohol	119°	61·6	5·5	$C_{17}H_{18}O_5N_2$	61·8	5·5	20
Cinnamovanillylamide	85	Prisms from alcohol	146—147 *	72·1	6·2	$C_{17}H_{17}O_3N$	72·1	6·1	0·5
$\alpha\beta$-Dichloro-β-phenylpropiovanillylamide	60	Nodular clusters of prismatic needles from alcohol	164—165	57·8	5·1	$C_{17}H_{17}O_3NCl_2$	57·6	4·8	3
Chloroacetovanillylamide	76	Thick prisms from alcohol	119—122 †	52·3	5·3	$C_{10}H_{12}O_3NCl$	52·3	5·3	3
Dichloroacetovanillylamide	75	Thick prisms from alcohol	139—143	45·5	4·3	$C_{10}H_{11}O_3NCl_2$	45·5	4·2	3
Trichloroacetovanillylamide	56	Plates from a mixture of alcohol and ether	76—79	40·0	3·4	$C_{10}H_{10}O_3NCl_3$	40·2	3·4	3
Bromoacetovanillylamide	28	Small needles from alcohol	94—95	44·0	4·6	$C_{10}H_{12}O_3NBr$	43·8	4·4	3
Iodoacetovanillylamide	100	Thick prisms from alcohol	114	37·5	3·9	$C_{10}H_{12}O_3NI$	37·4	3·8	3

* Nelson, not sharp; Ott and Zimmermann, 138°.

† Einhorn, 116—119°.

Substance.	Yield in per cent. of theory.	Crystalline form and solvent employed for crystallisation.	M. p. (corr.).	Analysis Per cent. C.	Analysis Per cent. H.	Formula.	Required. Per cent. C.	Required. Per cent. H.	Pungency.
n-Nono-3 : 4-dihydroxybenzylamide	68	Leaflets from chloroform	78°	68·7	9·1	$C_{16}H_{25}O_3N$	68·8	9·0	25
$\Delta\omega$-Undeceno-3 : 4-dihydroxybenzylamide	70	Microscopic needles from ether	70—74	70·6	8·9	$C_{18}H_{27}O_3N$	70·8	8·9	50
n-Nono-3 : 4-methylenedioxybenzylamide	—	Leaflets from ether	92	70·0	8·7	$C_{17}H_{25}O_3N$	70·1	8·7	0
n-Nono-4-hydroxybenzylamide	87	Leaflets from alcohol	92	72·8	9·8	$C_{16}H_{25}O_2N$	72·9	9·6	10
$\Delta\omega$-Undeceno-4-hydroxybenzylamide	31	Small needles from ether	92*	74·4	9·3	$C_{18}H_{27}O_2N$	74·7	9·3	30
n-Nono-4-methoxybenzylamide	—	Leaflets from ether	103	73·4	9·8	$C_{17}H_{27}O_2N$	73·6	9·8	0

* Ott and Zimmermann, 86°.

Small quantities of the dibenzylamines, divanillylamine and dianisylamine, were obtained as by-products of the reduction of the corresponding oximes, just as in the reduction of veratraldoxime (Rügheimer and Schön, *Ber.*, 1908, **41**, 17) and of benzaldoxime (Paal and Gerum, *Ber.*, 1909, **42**, 1553).

Vanillylamine hydrochloride melted at 227° (corr.) and gave with sodium hydroxide (1 mol.) the free base, which contained $2H_2O$. After drying over sulphuric acid, it melted at 145—146° (corr.). Nelson gives the m. p. of the dry substance as 131—133°, but it appears from the context that he dried it at 110°.

Divanillylamine hydrochloride, m. p. 244° (corr.), may be purified by crystallisation from water, in which it is much less readily soluble than vanillylamine hydrochloride (Found: C, 58·8; H, 6·3. $C_{16}H_{19}O_4N,HCl$ requires C, 58·9; H, 6·2%).

On the addition of the equivalent quantity of sodium hydroxide to its concentrated aqueous solution, *divanillylamine* was deposited in fine needles, which, after dehydration over sulphuric acid, melted at 92° and decomposed at 104° (corr.) (Found: C, 66·3; H, 6·8. $C_{16}H_{19}O_4N$ requires C, 66·4; H, 6·6%).

Piperonylamine hydrochloride melted at 247° (corr.). Mannich and Kuphal (*Ber.*, 1912, **45**, 318) give 227° (not sharp).

Anisylamine hydrochloride melted at 244° (corr.). Tiffeneau (*Bull. Soc. chim.*, 1911, **9**, 819) gives 240—241°.

In its preparation, the sparingly soluble dianisylamine hydrochloride was obtained as a by-product (Found: C, 65·5; H, 6·9. Calc., C, 65·4; H, 6·9%). This salt had m. p. 255° (corr.) and the base 34° (corr.); Steinhart (*Annalen*, 1887, **241**, 233) gives 243° and 34°, respectively.

p-Hydroxybenzylamine melted at 109° (corr.) after dehydration in a vacuum; Salkowski (*Ber.*, 1889, **22**, 2142) states that it melts in its water of crystallisation at about 95°.

3 : 4-Dihydroxybenzylamine hydrochloride is obtained in almost theoretical yield by heating vanillylamine hydrochloride (10 g.) with hydrochloric acid (20 c.c. conc.) for 5 hours at 140°. On the addition of slightly less than one equivalent of sodium hydroxide to its concentrated aqueous solution, in an atmosphere of hydrogen, 3 : 4-*dihydroxybenzylamine* is deposited in brown, sandy, anhydrous crystals, m. p. 158° (corr.; decomp.) (Found: C, 60·1; H, 6·7. $C_7H_9O_2N$ requires C, 60·4; H, 6·5%).

The Acids.—α-iso*Propyl*-n-*hexoic acid.* A mixture of ethyl *iso*propylmalonate (1 mol.), *n*-butyl bromide (1 mol.), and sodium ethoxide (1 mol.) in absolute alcohol was kept for several hours, and then boiled for 1 hour under reflux. The product was isolated in the usual way, and hydrolysed with alcoholic potash, when

iso*propyl*-n-*butylmalonic acid* was obtained in good yield. It formed hard prisms from absolute alcohol, m. p. 105° (corr.) (Found : C, 59·1; H, 9·0. $C_{10}H_{18}O_4$ requires C, 59·4; H, 9·0%).

On distillation, it gave α-iso*propyl*-n-*hexoic acid* as an oil, b. p. 220—225°, in a yield amounting to 77% of the theoretical calculated upon the ethyl *iso*propylmalonate used.

On treatment with phosphorus pentachloride (1 mol.) in chloroform, it gave the acid chloride, b. p. 155—158°, which gave with ammonia α-iso*propyl*-n-*hexoamide*, small, fatty plates from chloroform, m. p. 93° (corr.) (Found : C, 68·5; H, 12·2. $C_9H_{19}ON$ requires C, 68·7; H, 12·2%).

Undecenoic acid is obtained together with heptaldehyde by distilling castor oil under diminished pressure. The process was first described by Krafft (*Ber.*, 1877, **10**, 2034), whilst Becker (*Ber.*, 1878, **11**, 1412) states that the yield is about 10%, and Leeds (*Ber.*, 1883, **16**, 290) that the distillation is conducted under a pressure of 100 mm. Ott and Zimmermann (*loc. cit.*) obtained a greatly improved yield by distilling the oil through a red hot platinum spiral under 1 mm., cooling the receiver to — 80°, but these elaborate precautions are quite unnecessary, for a good yield may be obtained as follows.

Castor oil (300 g. B.P. quality) is distilled under 10 mm., the receiver being cooled to — 8°. Distillation begins when the temperature of the liquid reaches 293°, and this temperature remains stationary, whilst the temperature of the vapour rises from 140—175°. The rate of heating is controlled so that the temperature of the vapour does not exceed 175°. After about 2½ hours, distillation ceases, and the distillate is redistilled under 10 mm., heptaldehyde is collected at 45° and undecenoic acid at 150—170°. Yield 67 g. = 22·3% by weight of the oil.

δ-*Phenyl*-n-*valeric acid* may be prepared readily as follows : γ-Phenyl-*n*-propyl alcohol (20 g.) is converted quantitatively into γ-phenyl-*n*-propyl bromide by the method of Rupe and Bürgin (*Ber.*, 1910, **43**, 178) by means of phosphorus tribromide when 27 g. of the latter (in place of 20 g. as given by these authors) are employed. γ-Phenyl-*n*-propyl bromide (20 g.) was heated for 1 hour with the sodio-derivative of ethyl malonate (16 g.) in alcohol, and gave ethyl γ-phenyl-*n*-propylmalonate, b. p. 198°/10 mm.; yield 70%. This gave on hydrolysis γ-*phenyl*-n-*propylmalonic acid*, hard prisms from alcohol, m. p. 95° (corr.), which lost carbon dioxide at 160—170°, leaving δ-phenyl-*n*-valeric acid, m. p. 58°.

Preparation of Acylbenzylamides by Einhorn's Method.—Guaiacol and *N*-methylolbenzamide gave on condensation by Einhorn's method (*loc. cit.*, p. 235) a substance, m. p. 144—145° (corr.), in a yield of 27% (Einhorn gives m. p. 148° and yield not greater than

25%) which was identical (by the mixed melting-point method) with benzovanillylamide prepared by Nelson's method. *N*-Methylolbenzamide is best purified by crystallisation from chloroform; it then melts at 104° (Einhorn, 104—106°). We were unable to purify the substance by crystallisation from dilute alcohol, the method used by Einhorn.

Guaiacol and *N*-methylolchloroacetamide gave on condensation by Einhorn's method (*loc. cit.*, p. 292) a substance, m. p. 119—122° (corr.) (Einhorn, m. p. 116—119°), which was identical (by the mixed melting-point method) with chloroacetovanillylamide prepared by Nelson's method.

Guaiacol and *N*-methylolundecenoamide gave similarly a crude undecenovanillylamide, which was recognised as such by acetylation and isolation of O-*aceto*-N-*undecenovanillylamide*, needles from alcohol, m. p. 88° (corr.) (Found: C, 69·6; H, 8·6. $C_{21}H_{31}O_4N$ requires C, 69·5; H, 8·6%), which proved to be identical (by the mixed melting-point method) with the product of acetylation of undecenovanillylamide.

N-*Methylol*-Δ^{ω}-*undecenoamide*.—Five grams of undecenoamide, m. p. 87° (corr.) (Aschan, *Ber.*, 1898, **33**, 2349, gives 84·5—85·5°), formaldehyde (2·5 g. of 40% solution), and potassium carbonate (0·2 g.) in water (10 c.c.) are warmed and thoroughly mixed until the solution becomes clear. After keeping for 2 days, the separated crude *N*-methylolundecenoamide, m. p. 74—76°, is collected (yield 96%). It is recrystallised from acetone, the first crop, containing some unchanged undecenoamide, being rejected. The pure substance melts at 77° (corr.) (Found: C, 67·4; H, 11·0. $C_{12}H_{22}O_2N$ requires C, 67·5; H, 10·9%).

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CCCLVI.—*The Equilibrium in the Systems Aluminium Sulphate–Copper Sulphate–Water and Aluminium Sulphate–Ferrous Sulphate–Water at 25°.*

By VINCENT JOSEPH OCCLESHAW.

THIS investigation was commenced to determine by means of a phase-rule study the conditions under which aluminium sulphate forms "pseudo-alums," $Al_2(SO_4)_3,M''SO_4,24H_2O$, with the sulphates of such bivalent metals as magnesium, zinc, copper, manganese, and iron. When a large part of the work had been carried out, Caven and Mitchell (this vol., p. 527) published their results for the systems aluminium sulphate–copper sulphate–water and aluminium

sulphate–manganous sulphate–water at 30°. As the author has no intention of investigating further systems of this type, the work so far completed is being described.

Caven and Mitchell (*loc. cit.*) have shown that no double salt exists in the copper sulphate system at 30°. The double salt $Al_2(SO_4)_3,FeSO_4,24H_2O$, called "halotrichite" or "feather-alum," is a naturally-occurring, so-called "pseudo-alum," having been found by Forchlamner as a volcanic efflorescence in Iceland. Patterson (J., 1896, **69**, 66) found a salt approximating in composition to the above formula in wool-bleaching chambers, and the salt was prepared in presence of a large excess of sulphuric acid by Klauer (*Annalen*, 1835, **14**, 261). Wirth also (*Z. angew. Chem.*, 1913, **26**, 181), who made an incomplete study of the ferrous sulphate system, prepared this salt.

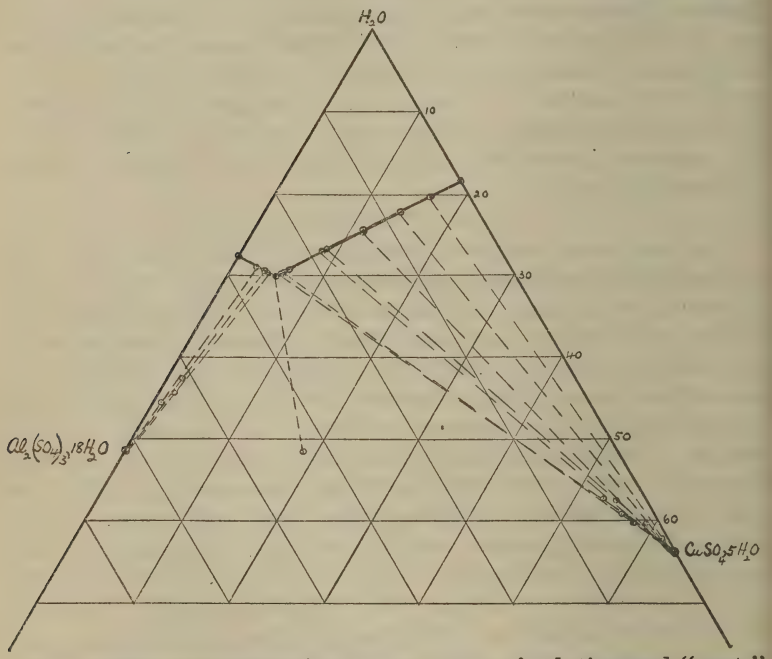
Experimental.

The aluminium sulphate was recrystallised before use. The copper sulphate and ferrous sulphate were "guaranteed chemicals" purchased from Messrs. Hopkin and Williams. Weighed quantities of the salts, which were more than sufficient to give saturated solutions, were placed with water in well-stoppered bottles in the case of the copper sulphate system and in hard glass tubes with tightly fitting rubber stoppers in the case of the ferrous sulphate system. These bottles and tubes were rotated in a thermostat regulated at 25° ± 0·1° until equilibrium was attained. The water used for the ferrous sulphate system was boiled previously to remove dissolved air and cooled in a current of hydrogen. In this case the tubes were charged in an atmosphere of hydrogen and all air was replaced by hydrogen before they were closed. Oxidation of the ferrous sulphate and subsequent separation of ferric hydroxide were thus prevented, but when the ferrous sulphate content of the solutions was fairly high some difficulty was experienced in preventing oxidation. By commencing with solid salts and water, the amount of hydrolysis of aluminium sulphate, as noted by Britton (J., 1922, **121**, 982), was so small that it could be neglected. Usually about a week elapsed before equilibrium was reached, but shaking was continued for a further period in all cases and a second analysis made. In both systems the resulting liquid phase was drawn quickly by suction through a cotton-wool filter into a warmed pipette and transferred to a weighing-bottle. The solid phase was drained by suction and the moist solid transferred to a weighing-bottle. After weighing, both liquid and solid phases were made up to known volumes with water and analysed.

Copper sulphate was estimated iodometrically and aluminium sulphate calculated by difference after determination of the total

sulphate. Ferrous sulphate was estimated by means of permanganate and aluminium sulphate calculated as above. The sulphate estimation was carried out in hydrochloric acid solution as recommended by Moser and Kohn (*Z. anorg. Chem.*, 1922, **122**, 299) and by Britton (*loc. cit.*) when aluminium is present. Almost every result was duplicated.

FIG. 1.



The results are expressed as g. per 100 g. of solution and "rest" respectively.

$Al_2(SO_4)_3$–$CuSO_4$–H_2O.

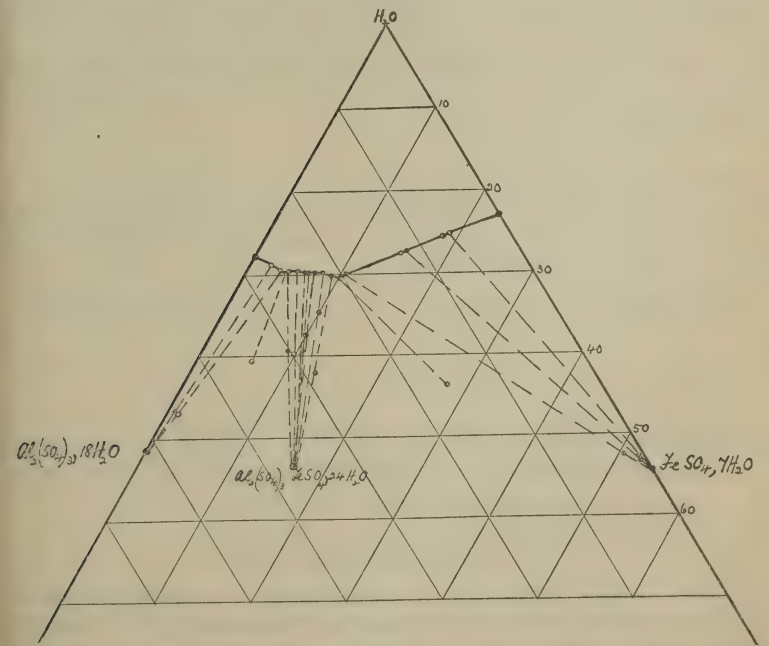
Solutions.			Rests.		
$Al_2(SO_4)_3$.	$CuSO_4$.	H_2O.	$Al_2(SO_4)_3$.	$CuSO_4$.	H_2O.
27·80	—	72·20	—	—	—
26·60	2·50	70·90	44·39	0·87	54·74
25·66	3·75	70·59	41·28	1·58	57·14
25·64	3·83	70·53	42·59	1·49	55·92
24·86	5·18	69·96	32·62	18·92	48·46
24·65	5·32	70·03	4·32	52·91	42·77
24·32	5·36	70·32	3·42	56·56	40·02
23·18	6·11	70·71	—	—	—
18·83	8·18	72·99	3·14	57·19	39·67
18·10	8·75	73·15	4·21	54·68	41·11
13·05	11·33	75·62	3·12	54·41	42·47
7·50	14·69	77·81	1·15	59·16	39·69
3·79	16·59	79·62	0·65	61·55	37·80
—	18·49	81·51	—	—	—

These results are plotted in Fig. 1, from which it will be seen that there is no double-salt formation in the copper sulphate system.

$Al_2(SO_4)_3$–$FeSO_4$–H_2O.

Solutions.			Rests.		
$Al_2(SO_4)_3$.	$FeSO_4$.	H_2O.	$Al_2(SO_4)_3$.	$FeSO_4$.	H_2O.
27·80	—	72·20	—	—	—
26·75	2·11	71·14	45·60	0·74	53·66
25·64	3·85	70·51	45·24	1·31	53·45
25·41	4·13	70·46	34·74	5·91	59·34
25·21	4·19	70·60	30·15	9·07	60·78
23·90	5·57	70·53	29·84	9·90	60·26
23·45	6·28	70·27	29·25	10·56	60·19
23·20	6·60	70·20	28·80	10·48	60·72
22·64	7·12	70·24	27·28	9·95	62·77
21·62	8·06	70·33	24·48	9·87	65·65
20·80	9·36	69·84	28·88	13·11	58·01
20·16	10·17	69·67	15·68	27·87	56·47
19·37	10·60	69·98	2·09	50·42	47·49
12·29	15·05	72·66	—	—	—
11·51	15·57	72·89	0·70	52·41	46·89
6·98	18·68	74·34	—	—	—
6·06	19·14	74·80	0·45	52·20	47·35
—	22·98	77·02	—	—	

FIG. 2.



These results are plotted in Fig. 2, from which it will be seen that in the ferrous sulphate system a double salt with composition corresponding to $Al_2(SO_4)_3$,$FeSO_4$,$24H_2O$ exists.

The results obtained for this system differ somewhat from those obtained by Wirth (*loc. cit.*). The area of existence of double salt is rather greater than that determined by him, and his solutions prove to be supersaturated when compared with the corresponding ones of Fig. 2. In trying to confirm his results, some of the solutions were shaken for periods varying from 2 to 8 weeks, but the results obtained were always in agreement with those given above within the range of experimental error.

In Fig. 2, the line joining the point representing pure water and that representing the double salt $Al_2(SO_4)_3,FeSO_4,24H_2O$ cuts the double-salt curve. Therefore it should be possible to crystallise the double salt from water. To test this deduction, which is in conflict with conclusions drawn by Wirth, a solution of equimolecular quantities of aluminium sulphate (22·2 g.) and ferrous sulphate (9·3 g.) in 30 c.c. of water (which had been previously boiled and cooled in a current of hydrogen) was kept in the thermostat at 25°. Dry, filtered air was drawn over the surface of the solution until sufficient solid separated out. This was sucked as dry as possible, washed with alcohol and then ether, and dried in air (Found : $FeSO_4$, 16·4; SO_4, 41·9. $Al_2(SO_4)_3,FeSO_4,24H_2O$ requires $FeSO_4$, 16·4; SO_4, 41·5%). The salt so obtained appeared to consist of fine, white needles having a silky appearance which matted together, especially on filtration, to give a solid, not unlike asbestos in appearance.

The author desires to express his thanks to Professor E. C. C. Baly, C.B.E., F.R.S., for granting facilities for carrying out this work, to Mr. D. M. Edwards, M.C., B.Sc., for the interest he has taken in it, and to Professor R. M. Caven, D.Sc.

THE UNIVERSITY OF LIVERPOOL. [*Received, September* 14*th*, 1925.]

CCCLVII.—*The Effect of Gum Arabic and other Emulsifiers on the Acid Hydrolysis of Esters in Heterogeneous Systems.*

By ROBERT CHRISTIE SMITH.

INVESTIGATIONS of the hydrolysis of methyl acetate in a homogeneous system containing agar-agar (Reformatsky, *Z. physikal. Chem.*, 1891, **7**, 34), gum arabic (Pearce and O'Leary, *J. Physical Chem.*, 1924, **28**, 51; compare, however, Shukov and Stschoukarev, *ibid.*, 1925, **29**, 285), or gelatin (Callow, *Trans. Faraday Soc.*, 1915,

11, 55) seemed to show that the presence of the colloid had little or no effect on the rate of hydrolysis.

The hydrolysis taking place in a heterogeneous system, the reactants being distributed between two immiscible phases, in presence of such substances as gums and other emulsifiers has now been studied.

The predictions of theory for a heterogeneous reaction have already been confirmed by Goldschmidt and Messerschmitt (*Z. physikal. Chem.*, 1899, **31**, 235), but it is possible that in presence of emulsifying agents some deviation may occur. Haworth and Lapworth (J., 1921, **119**, 765), in the reduction of nitro-compounds by aqueous ammonium sulphide, obtained an increased yield by emulsifying. As, however, the emulsifier might have acted as a catalyst, care must be exercised in drawing conclusions from their results. The experiments of the author show that some emulsifiers do expedite certain heterogeneous reactions and that their action is not catalytic. For example, the rate of hydrolysis of ethyl acetate in hydrochloric acid was 0·00562 c.c. (of *N*-solution) per minute in the absence of gum tragacanth and 0·00482 in its presence, whereas, in a heterogeneous system, the rate in presence of the gum was very nearly doubled. Had the effect of the gum tragacanth been partly catalytic the rate of hydrolysis of the ester in homogeneous solution also should have increased. Similarly with dammar; in its presence, the rate increased in the heterogeneous system, but declined to 0·00434 in the homogeneous system.

The reaction chosen first for study was the hydrolysis of ethyl acetate, dissolved in benzene, by hydrochloric acid in presence of the following emulsifiers at concentrations ranging from 0·01% to 10% : *Gums*, etc.—arabic, tragacanth, copal, dammar, mastic, sandarac, gelatin, isinglass, soluble starch—*Solids*—lamp black, blood charcoal, kaolin, fuller's earth, pumice, gypsum, barium sulphate, sulphur.

In the case of the solids, irrespective of their solubility in water and benzene, the rate of hydrolysis varied but slightly, being sometimes above and sometimes below the normal value; for sulphur, it increased at first and then diminished. In no case, however, did the deviation from the normal rate exceed 15%.

In the case of the gums, some striking results were obtained, especially with tragacanth and dammar, the normal rate being increased one and a half times by the latter, and being more than doubled by the former, at a concentration of 1%. With 0·1% arabic, a slight increase was noticed, but the rate became slower with increasing concentration. The rate was diminished by gelatin and isinglass, not appreciably affected by mastic and sandarac,

and increased by soluble starch. As the concentration of tragacanth increased, the rate increased, even after sufficient gum was present to absorb all the hydrochloric acid. This result suggests a specific absorption of both reactants. Another factor, however, must be operating, otherwise gum tragacanth should increase the rate of hydrolysis of an ester in homogeneous solution. As the observed rate in the heterogeneous system depends on the concentration of the ester in the aqueous phase, it is suggested that the partition coefficient is materially altered by tragacanth and dammar; the former, owing to its absorbent nature, drawing more ester into the aqueous phase, and the latter, owing to its solubility in benzene, lowering that of the ester.

Similar results were obtained with other esters and some of the emulsifiers mentioned above (see table).

Experimental.

Five c.c. of N-hydrochloric acid at 25° were added to a weighed quantity of the emulsifying agent (ground to pass a 150-mesh sieve) in a ground-stoppered glass bottle of about 250 c.c. capacity, previously warmed to 25°. Ten c.c. of $N/2$-ethyl acetate (N in the case of ethyl propionate and propyl acetate) in benzene were added, and the bottles placed in a rotary shaker of constant speed in a thermostat at 25°. At various intervals, after 200 minutes from the commencement, a bottle was withdrawn and cooled in ice-water for a minute in order to prevent any of the reactants being blown out on removal of the stopper; the whole contents were then titrated with standard baryta solution and phenolphthalein.

The percentage of the emulsifier is given as percentage of the total weight of the emulsion. Gums dispersible in water were left over-night with the hydrochloric acid. Blanks were always made to determine if there was any appreciable hydrolysis of the gum itself. The lamp-black was purified by heating to redness, treating with hydrochloric acid, and washing with water. The fuller's earth was treated with hydrochloric acid to remove the carbonate present, and then washed till acid-free. It was found easier to neutralise the hydrochloric acid present with sodium hydroxide free from carbonate and complete the titration with baryta.

In the heterogeneous reactions, during the first 5 hours, only a small fraction of the ester was hydrolysed. It is therefore sufficiently accurate to calculate x/t, where x = number of c.c. of N-ester hydrolysed in t minutes. Readings were never taken more than 6 hours from the commencement of the experiment. Hence the

constants in the table represent the average number of c.c. of a N-solution of the ester hydrolysed per minute. The constants for the homogeneous reactions were calculated in the usual manner, the unit of time being the minute. Two sets of determinations were made and the results of each set usually agreed within 3%.

TABLE I.

Ester.	Normal.	Arabic.	Traga-canth.	Dammar.	Kaolin.
Ethyl acetate	0·0014	0·0012	0·0024	0·0020	0·0016
Propyl acetate ...	0·00067	0·00064	0·00093	0·00086	0·00071
Ethyl propionate...	0·00076	0·00077	0·00096	0·00099	0·00079

The author takes this opportunity to thank the Carnegie Trustees for a grant which enabled the research to be carried out.

UNIVERSITY OF GLASGOW. [*Received, June 16th*, 1925.]

CCCLVIII.—*An Investigation of the Effect of Differential Aëration on Corrosion by means of Electrode Potential Measurements.*

By A. L. MCAULAY and F. P. BOWDEN.

IN a recent paper (American Chemical Society Corrosion Symposium, 1925; *Ind. Eng. Chem.*, 1925, **17**, 363), Evans discusses oxygen distribution as a factor in the corrosion of metals. The present investigation was undertaken with the object of measuring the potentials between solution and metal in the various zones recognised by Evans on a metal corroded by a partly aërated solution. The potential differences in different zones were very clearly distinguished and on attempting to co-ordinate the results by measurements on standard surfaces it was found that the method provided a sensitive means of detecting the commencement of corrosion and recognising the state of the surface.

EXPERIMENTAL.

In the first set of experiments the method of preparing the specimens described by Evans was adopted. Sheets of zinc and iron were partly immersed in $N/10$-sodium chloride and, after 24 hours, their surfaces were studied. Following Evans, four distinct zones were recognised on the corroded specimen: (1) A zone unwetted by the solution. (2) A zone over which the solution has crept, necessarily well aërated. (3) A zone beneath, but close to the surface of the solution, also well aërated. (4) A zone of deficient aëration at greater depths.

Zones 1, 2, and 3 were bright and zone 4 was more or less badly corroded. Measurements were made of the single electrode potential between $N/10$-sodium chloride and the various zones.

In the second set of experiments the single electrode potentials between $N/10$-sodium chloride and standard surfaces were measured under differing conditions. These surfaces were extremely sensitive to exposure either to air or to electrolyte; *e.g.*, to obtain the true potential of freshly deposited electrolytic zinc, it was necessary carefully to plate the whole of the exposed surface, wash with water, and measure the electrode potential before the zinc had completely dried. If the surface were allowed to become dry for more than a few minutes, its electrical character changed completely.

Broadly classified, all the surfaces were electrically in one of two standard conditions, and the rapid changes were from one to the other of these standard conditions.

Method of Measurement and Apparatus.—Two distinct methods of measurement were used. In the " A " method the specimen was dry and the single electrode potential was measured between the metal and a drop of $N/10$-sodium chloride of about $\frac{1}{2}$ mm. diameter placed on the metal surface. It is necessary that the drop be very small, as otherwise the effects of corrosion by the drop are marked owing to differential aëration. This type of measurement gives the true single electrode potential between solution and metal.

In the " B " method of measurement the specimen, or the region under investigation, was flooded with sodium chloride solution or with water, or occasionally was immersed to a depth of 0·5 cm. in the solution, and the potential difference between the electrolyte and the metal surface was measured at different places. This type of measurement gives the electrical conditions while corrosion is in progress.

In the case of iron, the specimens prepared by Evans's method were not allowed to dry, but were kept wet with water; this was necessary on account of the rapid decrease in the electrode potential of the corroded portion on exposure to air.

The measurements were made against a normal calomel electrode, *A* (Fig. 1). This communicated with a tube, *B*, filled with $N/10$-sodium chloride, the end of which was drawn out to a hollow tip with a diameter of about $\frac{1}{2}$ mm. This tip made contact with the solution above the metal plate, *C*. The potential difference between the mercury of the calomel electrode and the metal plate was measured by a potentiometer. The apparatus was sensitive to a millivolt.

Experiments.—In the first series of experiments, specimens of zinc and iron were corroded by partial immersion in $N/10$-sodium

chloride for a period varying from 12 hours to 2 days. The results of measurements made on them by methods A and B are dealt with in the next section.

In the second series of experiments measurements were made by method A on the following standard surfaces :

Zinc, freshly deposited electrolytically.
Zinc, freshly polished with sandpaper.
Zinc, exposed to a well-aërated solution of $N/10$-sodium chloride for 2 days.

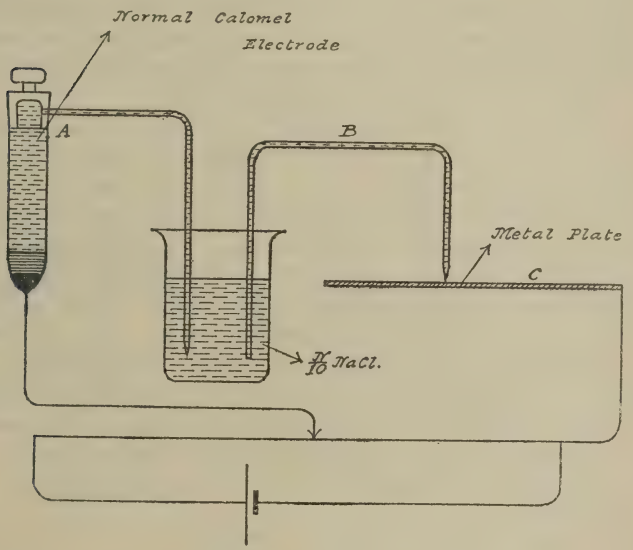


Fig. 1.

Zinc the surface of which had been exposed to air for a considerable time.
Zinc which had been heavily oxidised by heating.
Polished and oxidised iron surfaces were also examined.

As above mentioned, all these surfaces fell into one of two broad classes, one characteristic of freshly deposited metal which has never been exposed to air and the other characteristic of aërated surfaces. Under the influence of air, or differentially aërated electrolyte, one surface would pass rapidly from one class to the other.

In measuring the potential between standard surfaces and $N/10$-sodium chloride, it was found that the potential difference varied with the size of the drop. A small drop on a dry surface (with the

exception of dried zone 4 on zinc) gave the potential associated with one class, but if this drop were enlarged the potential immediately began to acquire the characteristic of that of the other class. This was found to be due to electrolytic action taking place between the well-aërated edge of the drop and its poorly aërated centre. The following measurements were made to confirm this result.

A large drop, from 1 to 2 cm. in diameter, was placed on a zinc surface for about a minute and then blotted off, and the potentials where the centre and the edge of the drop had rested were measured with a drop about $\frac{1}{2}$ mm. in diameter. The edge showed the potential characteristic of an aërated surface, and the centre, that characteristic of freshly deposited zinc. The latter very rapidly returned to its initial condition, and when measured was usually between the two conditions and falling rapidly.

To confirm further this result, two zinc surfaces were prepared to simulate under very different experimental arrangements the conditions existing in large and small drops on the zinc surface. The specimen corresponding to a large drop was partly immersed in electrolyte and corroded under conditions of differential aëration. The potential of zone 4 was the same as the highest value obtained for the centre of the drop, but the zone, when visibly corroded, did not return to the aërated state for several days. The potential of zone 3 was that of the outside of the drop. The specimen corresponding to a small drop was immersed in electrolyte which was well aërated throughout by bubbling air through it. It remained uncorroded and its surface after treatment for more than 24 hours showed the potential characteristic of the small drop on a well-aërated surface.

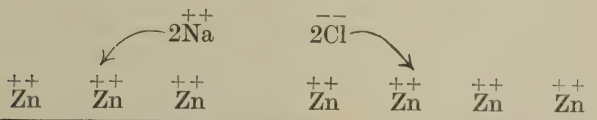
Discussion of Results.

In the corrosion of a metal immersed in an electrolyte, the metal shows an equi-potential surface owing to the small currents flowing. There is, however, a fall of potential down the solution, the positive regions being situated where the metal is most negative to the solution. Such a region corresponds exactly to the negative plate of a simple primary cell and is called anodic.

Figs. 2 and 3 summarise diagrammatically the general nature of the process that takes place. Chlorine ions move towards the anodic region under the influence of the electric field in the solution produced by the greater solution pressure in the corroded region. They there neutralise metallic ions, lowering the potential difference between solution and metal and enabling more metallic ions to leave the metal. These ions on emerging restore the potential difference. Sodium ions migrate to the ennobled region and are neutralised by electrons drawn from the metal.

As a broad generalisation, two types of surface may be recognised classified by the potential between them and $N/10$-sodium chloride. In the case of zinc the electrode potential of the first class against the normal calomel electrode is generally within 15 millivolts of $-1{\cdot}075$ volts, but may be more negative still where the corrosion is heavy. Fresh electrolytically deposited zinc and zone 4 of the corroded metal are in this class. They are the less noble regions on the corrosion specimens, or the more anodic. The second class comprises zones 1, 2, and 3 on corroded specimens, surfaces freshly polished with sandpaper, specimens exposed to uniformly aërated electrolyte, and all surfaces which have been exposed to air for more than a few minutes, with the exception of zone 4 on corroded specimens, which remains in the first class even after prolonged

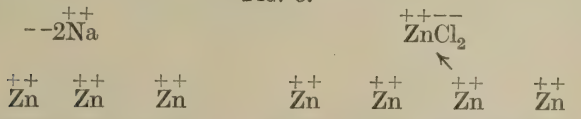
FIG. 2.



Oxidised surface. Potential difference $-1{\cdot}000$ volt.

Corroded surface. Potential difference $-1{\cdot}075$ volt.

FIG. 3.



Oxidised surface.

Corroded surface.

exposure to air. This second class of surface gives an electrode potential against the calomel electrode within about 15 millivolts of $-$ 1·000 volt. Values considerably less negative than this are obtained with specimens oxidised by heating in air. Surfaces in this second class are the more noble regions on the corroded specimens.

In the case of iron, few measurements against standard surfaces have been made. Measurements on corroded specimens and on polished specimens show the same general effects as with zinc, the two classes of surface described above being recognised and occurring under similar conditions. The first class has a potential difference against the calomel electrode of about $-$ 0·540 volt, the second class has a potential against the calomel electrode of $-$ 0·340 volt. Iron surfaces of the first class, on exposure to air, very rapidly change to the second class. This is true for zone 4 in iron, which in zinc remains true to type when exposed to air.

Figs. 4 and 5 show, diagrammatically, corroded specimens of zinc and iron, respectively. The potential differences as measured by method A against the calomel electrode are shown on the figures. All these potentials given against the calomel electrode include the contact *E.M.F.* due to the liquid junction *N*-KCl–*N*/10-sodium chloride. No attempt was made to standardise this contact, and capillary tubes and plugs of filter-paper were included in the circuit. It is the relative rather than the absolute potentials of these zones which are of value.

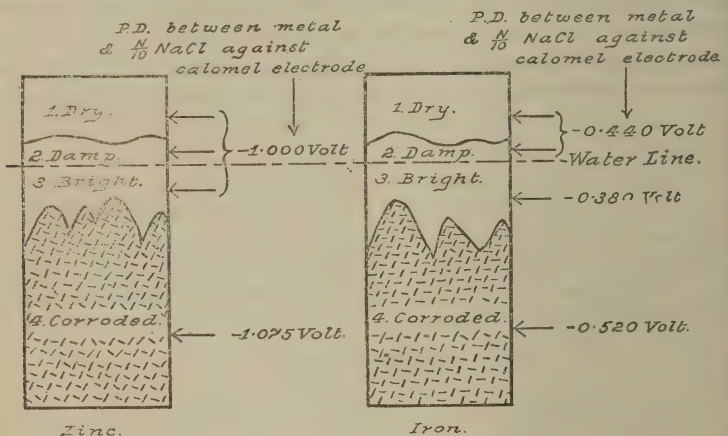


Fig. 4. *Fig. 5.*

The principal results of the investigation may therefore be summarised as follows: There are two normal states in which iron and zinc surfaces tend to exist, one a more electro-negative state characteristic of pure metal and corroded regions, the other a less electro-negative state, characteristic of aërated regions. For zinc, the difference in single electrode potential between these states is about 75 millivolts; for iron, it is about 200 millivolts. By drastic treatment (heavy corrosion in the first case, heavy oxidation in the second) the potentials in these states become more negative and more positive respectively. When drastically treated, the surfaces are visibly heavily corroded, and, in the case of zinc, do not rapidly change their condition without further drastic treatment. Experiments with drops have shown that surfaces having a clean bright appearance may be in either of the two states and then very rapidly change from one state to the other with change of conditions.

UNIVERSITY OF TASMANIA,
HOBART.

[*Received, August 7th*, 1925.]

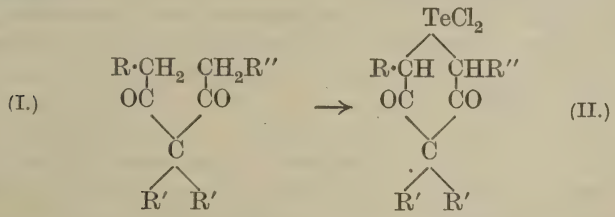
CCCLIX.—*Production of* cyclo*Telluripentanedione Dichlorides.*

By GILBERT T. MORGAN.

[With FREDERICK JAMES CORBY, OLIVER CECIL ELVINS, EVELINE JONES, RICHARD EATOUGH KELLETT, and CYRIL JAMES ALLAN TAYLOR.]

THE search for co-ordination derivatives of tellurium and the β-diketones led to the discovery of two new groups of cyclic tellurium compounds in which the diketone concerned furnishes a bivalent chelate group. These cyclic substances are not the sole products of the condensation of tellurium tetrachloride with β-diketones, and certain of the diketones examined have not given them, but as the result of numerous experiments it now becomes possible to predict with a fair degree of certainty which β-diketones are likely to furnish the chelate groups required to implicate tellurium in the six-membered rings.

Certain constitutional features must be present in a β-diketone in order that it may function in the desired sense, and within the limits imposed by these structural requirements the reaction is a general one.



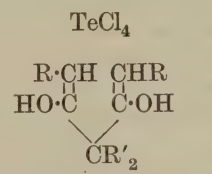
Formula I represents any β-diketone which would condense with tellurium tetrachloride to produce a cyclic telluridichloride (II), provided that the substituents R, R′, and R″ are of the appropriate chemical type.

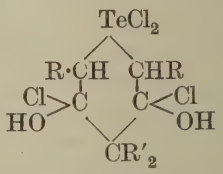
Acetylacetone, the simplest case, where R = R′ = R″ = H, gives as the main product *cyclo*telluripentane-3 : 5-dione 1 : 1-dichloride (formula II). It has, however, also yielded two other products both of which are non-cyclic; the first of these is the telluritrichloride, $CH_3{\cdot}C(OEt){:}CH{\cdot}CO{\cdot}CH_2{\cdot}TeCl_3$, obtained by the intervention of ethyl alcohol present in ordinary chloroform, the second is a telluridichloride which is still enolic,

$$\{CH_3{\cdot}C(OH){:}CH{\cdot}CO{\cdot}CH_2\}_2TeCl_2.$$

These by-products arise evidently from interaction between tellurium tetrachloride and acetylacetone in its monoenolic form induced

by migration of hydrogen from the median carbon atom. It is, however, highly probable that the main cyclic product is due to condensation with a dienolic modification, $CH_2{:}C(OH)\cdot CH_2\cdot C(OH){:}CH_2$, developed by twofold enolisation from the two terminal hydrocarbon radicals. The process probably takes place in two stages, the tellurium tetrachloride first combining additively with the dienolic modification of the β-diketone, giving rise to the hypothetical addition product (IV), which by subsequent loss of two molecules of hydrogen chloride passes into the stable *cyclo*telluridichloride (II).

(III.) 



(IV.)

It is of general interest in connexion with dynamic isomerism that in these condensations the tetrachlorides of selenium and tellurium behave dissimilarly and evoke a different response from the reacting tautomeric diketone. Selenium tetrachloride attacks the monoenolic isomeride produced by median enolisation or its analogously constituted copper derivative. Tellurium tetrachloride links up the unsaturated ends of a five-membered chain arising from twofold terminal enolisation. This explanation of the mechanism of the tellurium condensation is supported by the following experimental evidence.

1. *Median enolisation.* So long as 2R′ in the foregoing formulæ represent two hydrogen atoms there is considerable tendency for one of these to migrate to an adjacent oxygen atom, thus giving rise to median enolisation. The result of this dynamic change in the case of acetylacetone has already been mentioned; it leads to two non-cyclic products. Similar non-cyclic products have been noticed with propionylacetone, dipropionylmethane, di-*n*-butyrylmethane, and hexoylacetone. The last two diketones exhibit the interesting case of an enolic non-cyclic telluritrichloride,

$\{C_2H_5\cdot CH_2\cdot C(OH){:}CH\cdot CO\cdot CH(C_2H_5)\}TeCl_3$ and

$\{C_5H_{11}\cdot CH_2\cdot C(OH){:}CH\cdot CO\cdot CH_2\}TeCl_3$.

It is probable that the three types of non-cyclic tellurium compounds (*O*-ethyl-trichloride and enolic trichloride and dichloride) may be present in other condensations with non-3-alkylated β-diketones, but that owing to instability and great solubility these products have not been isolated, the experimental difficulties becoming greater as the number of carbon atoms in the chain increases.

2. *Lengthening of the unbranched chain.* Providing that the tendency to terminal enolisation is not diminished by substitution of alkyl radicals for hydrogen in the reactive terminal methylene groups R·**CH$_2$**·CO·CH$_2$·CO·**CH$_2$**·R′, the lengthening of hydrogen chain R or R′ does not prevent the formation of a *cyclo*telluripentanedione derivative, and the general nature of the reaction has been demonstrated by condensing such higher ketones as *n*-octoylacetone, *n*-nonoylacetone, and *n*-duodecoylacetone (lauroylacetone) with tellurium tetrachloride. The last of these has yielded 2-n-*decyl*cyclo*telluripentane*-3 : 5-*dione* 1 : 1-*dichloride* (VII), reducible to 2-n-*decyl*cyclo*telluropentane*-3 : 5-*dione* (VIII).

Sufficient examples have been selected to show that the production of *cyclo*telluripentanedione dichlorides and their reduction to *cyclo*telluropentane-3 : 5-diones are general reactions for all β-diketones having structural formula I when R and R″ are normal or unbranched hydrocarbon chains.

3. *Alkylation of the median methylene group.* When one R′ is hydrogen and the other an alkyl group, the tellurium condensation becomes simplified so that, although many 3-alkylated β-diketones have been examined, only one telluriferous product has been identified in each case. The 3-alkylacetylacetones react smoothly and give 4-alkyl*cyclo*telluripentane-3 : 5-dione 1 : 1-dichlorides in good yield. The 3-*propylpropionylacetones* (normal and *iso*) described below behave similarly and give rise to the two isomeric 2-*methyl*-4-*propyl*cyclo*telluripentane*-3 : 5-*dione* 1 : 1-*dichlorides* (IV).

3-iso*Butylacetylacetone* also condenses smoothly with tellurium tetrachloride, yielding only one product, namely, the cyclic telluridichloride (II).

4. *Branched chains on the median carbon atom.* 3-*iso*Propylacetylacetone, $(CH_3)_2CH·CH(CO·CH_3)_2$, and 3-*iso*propylpropionylacetone, $(CH_3)_2CH·CHAc·CO·C_2H_5$, furnish interesting examples of the influence of chemical structure on median enolisation. They differ from their *n*-propyl isomerides in giving neither ferric nor cupric derivatives. 3-*iso*Butylacetylacetone,

$$(CH_3)_2CH·CH_2·CH(CO·CH_3)_2,$$

in which a methylene group is interposed between the branched chain and the median carbon atom, gives, however, both ferric and cupric derivatives just as readily as 3-*n*-butylacetylacetone (J., 1924, **125**, 763). But although ordinary median enolisation is inhibited in the 3-*iso*propyl-β-diketones, they react with tellurium tetrachloride to give cyclic telluridichlorides. If enolisation is an essential concomitant of the primary phase in this condensation, it is therefore more probably terminal than median.

5. 3 : 3-*Dialkylated* β-*diketones.* The fact that 3 : 3-dimethyl-

and 3 : 3-diethyl-acetylacetone both give cyclic telluridichlorides is conclusive evidence that any preliminary enolisation must be terminal, since in these cases the possibility of median enolisation is absent (Morgan and Drew, J., 1924, **125**, 735, 1601).

6. *Terminal branching chains.* In formula I the terminal chains are represented by the symbols $R{\cdot}CH_2$— and —CH_2R'', and it has been found that cyclic telluridichlorides are not produced unless both methylene groups are present. If cyclic condensation is prevented entirely by the conversion of one CH_2R group into CHRR′, the β-diketones with one such branching chain give only non-cyclic telluritrichlorides and dichlorides.

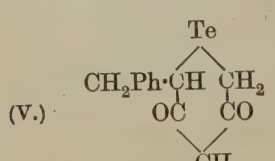
With two terminal branching chains, as in di*iso*butyrylmethane, the formation of telluriferous products is reduced to a minimum, 90% of the tellurium is set free, and the only telluriferous product is a non-cyclic telluritrichloride formed to a very slight extent (Morgan and Taylor, this vol., p. 797).

7. *Influence of aromatic groups.* Benzoylacetone is incapable of twofold terminal enolisation and gives rise only to non-cyclic telluriferous compounds, and for similar reasons ill-defined products are obtainable from dibenzoylmethane.

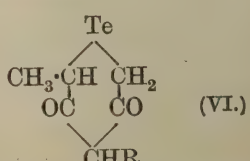
When present in the positions indicated by R, R′, and R″, phenyl radicals prevent completely the formation of *cyclo*telluridichlorides unless a methylene group is interposed. This intervention is effected at the median carbon atom by benzylating the sodium derivative of β-diketone as in 3-*benzylpropionylacetone*, which condenses to form 4-*benzyl*-2-*methyl*cyclo*telluripentane*-3 : 5-*dione* 1 : 1-*dichloride* (VI).

3-Benzyl- and 3 : 3-dibenzyl-acetylacetones have also been converted into cyclic telluridichlorides, although condensation did not occur with 3 : 3-di-*p*-nitrobenzylacetylacetone (Morgan and Taylor, *loc. cit.*).

A benzyl group was introduced into terminal position R or R″ (formula I) by operating with β-*phenylpropionylacetone*, which underwent condensation with tellurium tetrachloride in the normal way, for although the cyclic telluridichloride was not isolated in a state of purity, it was identified by conversion into its reduction product, 2-*benzyl*cyclo*telluropentane*-3 : 5-*dione* (V).



(V.)



(VI.)

R = *n*- or *iso*-C_3H_7 or CH_2Ph.

8. *Reduction of* cyclo*telluripentanedione dichlorides to* cyclo*telluropentanediones.* Apart from the chemical significance attaching to the new group of cyclic telluridichlorides, these derivatives are of interest from the point of view of chemical bacteriology, because each member of the group is readily reducible to a *cyclo*telluropentanedione (V and VI), the reaction being a general one. Many of these cyclic telluro-derivatives are sufficiently soluble in cold water to impart to the aqueous solutions outstanding germicidal properties. The most powerful bactericide of the series is 2 : 6-dimethyl*cyclo*telluropentane-3 : 5-dione (from dipropionylmethane), but as this derivative is difficult to produce in large amount the next most efficient members have been most extensively employed in bacteriological tests. These substances are 2-methyl*cyclo*telluropentane-3 : 5-dione (from propionylacetone) and its 3-alkylated homologues. The methyl and ethyl derivatives have already been prepared, whereas the *n*- and *iso*-propyl compounds and the benzyl derivatives, all symbolised by the general formula VI, are described in the experimental part of this communication.

9. *Oximes of* cyclo*telluropentane*-3 : 5-*diones.* The chemical constitution ascribed to *cyclo*telluropentane-3 : 5-diones (V and VI) as the result of the preceding experimental proofs is confirmed by the oximation of these substances.

In general, both monoximes and dioximes are obtainable, although it is evident that the progress of this reaction is affected by steric hindrance.

2-Methyl*cyclo*telluropentane-3 : 5-dione resembles *cyclo*telluropentane-3 : 5-dione, the simplest member of the series, in yielding chiefly the dioxime, whereas 2-methyl-4-ethyl*cyclo*telluropentane-3 : 5-dione yields both mono- and di-oximes and the monoxime is never entirely absent even when drastic oximation is employed. These examples and the earlier cases (Morgan and Drew, Morgan and Taylor, *loc. cit.*) demonstrate the presence of two ketonic carbonyl groups in the *cyclo*telluropentane-3 : 5-diones.

Experimental.

[With Frederick James Corby.]

1. 2-*Methyl*-4-*propyl*cyclo*telluropentane*-3 : 5-*dione* (VI).

Sodium propionylacetone (23 g.), made from the diketone in dry ether, was heated for 8 hours with 80 g. of *n*-propyl iodide; reaction commenced at 115°, the temperature was maintained at 130° for 2 hours, and finally raised to 150°. The cooled mixture was added to water, the aqueous layer extracted with ether, and the ethereal extract added to the organic layer. The latter on

fractionation furnished n-*propylpropionylacetone*, b. p. 210°/750 mm. with slight decomposition. This *n*-propyl diketone gave an intense bluish-purple coloration with ferric chloride quite distinct from the blood-red tints obtained with the non-3-alkylated diketones. The new diketone had a pleasant terpenoid odour and yielded with ammoniacal cupric acetate a greenish-grey, voluminous precipitate of *copper* 3-n-*propylpropionylacetone*, readily soluble in acetone, methyl and ethyl alcohols and crystallising from benzene in greenish-grey, silvery needles melting and decomposing at 178° (Found : Cu, 16·8. $C_{18}H_{30}O_4Cu$ requires Cu, 17·0%).

2-*Methyl*-4-n-*propyl*cyclo*telluripentane*-3 : 5-*dione* 1 : 1-*Dichloride*,

$$CH_3\cdot[CH_2]_2\cdot CH\!<\!\begin{matrix}CO\cdot CH_2\\ CO\cdot CH(CH_3)\end{matrix}\!>\!TeCl_2.$$

—After heating under reflux for 1½ hours a mixture of 6 g. of 3-*n*-propylpropionylacetone, 5·7 g. of tellurium tetrachloride, and 50 c.c. of chloroform, the orange filtrate from tellurium was concentrated in a vacuum over calcium chloride until crystals of the telluridichloride separated. The mother-liquor after extraction with light petroleum to remove unchanged diketone was again concentrated, and the process repeated so that three crops of crystals were obtained (yield 62%). Recrystallised from chloroform, the *dichloride* separated in colourless prisms darkening at 145°, blackening at 150° (Found : Cl, 20·2; Te, 35·9. $C_9H_{14}O_2Cl_2Te$ requires Cl, 20·2; Te, 36·15%).

When suspended in ice-cold water and treated with potassium metabisulphite, the dichloride was readily reduced to 2-*methyl*-4-n-*propyl*cyclo*telluropentane*-3 : 5-*dione* (VI), with slight deposition of tellurium. The product was soluble in water, but less soluble than its 3-methyl analogue; it was recovered from aqueous solution by benzene. It was obtained from methyl alcohol in golden-yellow crystals, m. p. 102° with slight decomposition (Found : C, 38·3; H, 5·1; Te, 44·9. $C_9H_{14}O_2Te$ requires C, 38·4; H, 5·0; Te, 45·2%).

2. 2-*Methyl*-4-iso*propyl*cyclo*telluropentane*-3 : 5-*dione* (VI).

Sodium propionylacetone (23 g.) was heated with 120 g. of *iso*propyl iodide for 8 hours at 130°. The cooled mixture was poured into water and the two layers were worked up as in the case of the *n*-propyl isomeride.

3-iso*Propylpropionylacetone*, $CH_3\cdot CH_2\cdot CO\cdot CH(CHMe_2)\cdot CO\cdot CH_3$, boiled at 195°/750 mm. with slight decomposition; it differed from 3-*n*-propylpropionylacetone in not developing any ferric coloration and in not giving a copper derivative with ammoniacal cupric acetate.

2-*Methyl*-4-iso*propyl*cyclo*telluripentane*-3 : 5-*dione* 1 : 1-*Dichloride*,

$$(CH_3)_2CH\cdot CH\!<\!\begin{matrix}CO\cdot CH_2\\ CO\cdot CH(CH_3)\end{matrix}\!>\!TeCl_2.$$

—Ten g. of the preceding diketone, 9 g. of tellurium tetrachloride, and 80 c.c. of purified chloroform were heated under reflux for 2 hours and the orange filtrate was concentrated to the crystallising point. The subsequent procedure was the same as in the case of the *n*-propyl isomeride, and the telluridichloride crystallised in colourless, glistening prisms darkening at 168° and blackening at 173° (Found : Cl, 20·1; Te, 35·8. $C_9H_{14}O_2Cl_2Te$ requires Cl, 20·2; Te, 36·17%).

Reduction in the normal way led, with liberation of free tellurium, to 2-*methyl*-4-iso*propyl*cyclo*telluropentane*-3 : 5-*dione* (VI); this product crystallised from methyl alcohol in light yellow needles, m. p. 127°; it was much less soluble in water than the corresponding *n*-propyl compound (Found : C, 38·5; H, 5·05; Te, 44·85. $C_9H_{14}O_2Te$ requires C, 38·4; H, 5·0; Te, 45·1%).

An attempt was now made to prepare a third isomeride of the foregoing isomeric propyltelluro-derivatives. 3-Methylpropionylacetone, prepared by the method formerly described (J., 1924, **125**, 745), was dissolved in dry ether and converted into sodium salt. The latter was heated with 3 parts of ethyl iodide in an autoclave for 6 hours at 180°, the pressure being 10 atmospheres. The dialkylated diketone was extracted from the mixture by the procedure adopted for the two propylated diketones. On fractionation, 3-*methyl*-3-*ethylpropionylacetone* distilled at 118°/10 mm. (yield 25%). The diketone, which had a fragrant odour, gave neither coloration with ferric chloride nor precipitate with ammoniacal cupric acetate.

In the condensation with tellurium tetrachloride and 3-methyl-3-ethylpropionylacetone, tellurium was deposited and a considerable amount of tar was produced; the telluridichloride was not isolated, although it was probably present in the brown, tarry chloroform solution, since this changed to bright yellow on treatment with aqueous metabisulphite.

3. 4-*Benzyl*-2-*methyl*cyclo*telluropentane*-3 : 5-*dione* (VI).

3-*Benzylpropionylacetone*.—Sodium propionylacetone (34 g.) was heated under reflux with 13 g. of rectified benzyl chloride for 8 hours at 140°, the product being worked up as in the case of the propylated diketones. The benzylated diketone, which distilled at 185°/20 mm., was a colourless liquid with fragrant odour; it developed an intense reddish-violet coloration with ferric chloride and with ammoniacal cupric acetate it yielded a *copper* derivative

readily soluble in alcohol, acetone, or benzene to dark olive-green solutions. *Copper* 3-*benzylpropionylacetone* crystallised from these solvents in pale grey, silvery needles, m. p. 182° (Found : Cu, 13·4. $C_{26}H_{30}O_4Cu$ requires Cu, 13·5%).

4-*Benzyl*-2-*methyl*cyclo*telluripentane*-3 : 5-*dione* 1 : 1-*Dichloride*,

$$C_6H_5{\cdot}CH_2{\cdot}CH{<}\begin{matrix}CO{\cdot}CH_2\\CO{\cdot}CH(CH_3)\end{matrix}{>}TeCl_2$$

—The orange solution obtained by heating 8·5 g. of 3-benzylpropionylacetone, 5·8 g. of tellurium tetrachloride, and 50 c.c. of dry chloroform for 2 hours was decanted from tellurium and concentrated in a vacuum to the crystallising point. The mother-liquor was treated as in the case of the propylated dichlorides, and 5 g. of telluriferous product were obtained. Recrystallised from acetone, the *telluridichloride* separated in colourless, glistening prisms, m. p. 168° (Found : Cl, 17·7; Te, 31·8. $C_{13}H_{14}O_2Cl_2Te$ requires Cl, 17·75; Te, 31·7%).

Suspended in water and reduced with potassium metabisulphite, the dichloride yielded 4-*benzyl*-2-*methyl*cyclo*telluropentane*-3 : 5-*dione* with very slight elimination of tellurium. This telluro-derivative crystallised from methyl alcohol in yellow needles, m. p. 124° with decomposition. The crystals did not sublime in a vacuum and were only slightly soluble in water (Found : C, 47·5; H, 4·4; Te, 38·4. $C_{13}H_{14}O_2Te$ requires C, 47·3; H, 4·3; Te, 38·8%).

[With Eveline Jones.]

1. 3-iso*Butylacetylacetone*, $(CH_3)_2CH{\cdot}CH_2{\cdot}CH(CO{\cdot}CH_3)_2$.

Rectified *iso*butyl iodide (b. p. 117—120°) was obtained in 60% yield by Blaise's method (*Bull. Soc. chim.*, 1911, **9**, 1). A mixture of 161 g. of this iodide and 52 g. of sodium acetylacetone contained in a stoppered glass bottle was heated gradually in a rotating autoclave to 170°, and was maintained at this temperature for an hour (pressure 150 lb. per sq. inch). The liquid contents of the bottle were drained from sodium iodide and unchanged sodium acetylacetone, and the latter solids were extracted with ether. The oil and ethereal extracts were distilled together up to 124° to remove solvent and *iso*butyl iodide, and the residue was fractionated under reduced pressure; the fraction distilling at 93—94°/10 mm. consisted of 3-iso*butylacetylacetone*, which developed a bluish-purple coloration with ferric chloride and was purified by conversion into its copper derivative by interaction with ammoniacal cupric acetate. *Copper* iso*butylacetylacetone* crystallised from petroleum (b. p. 80—80°) in well-defined, steel-grey needles, m. p. 158° (Found : Cu, 16·9. $C_{18}H_{30}O_4Cu$ requires Cu, 17·0%).

4-iso*Butyl*cyclo*telluripentane*-3 : 5-*dione* 1 : 1-*Dichloride*,

$$(CH_3)_2CH{\cdot}CH_2{\cdot}CH{<}\begin{matrix}CO{\cdot}CH_2\\CO{\cdot}CH_2\end{matrix}{>}TeCl_2.$$

—A mixture of 5·8 g. of *iso*butylacetylacetone and 5 g. of tellurium tetrachloride in 40 c.c. of purified dry chloroform was heated on the water-bath for 1—2 hours. The filtrate from a small deposit of tellurium was concentrated at the ordinary temperature until acicular crystals separated. Recrystallised from acetone or chloroform, the *dichloride* separated in well-defined, colourless needles, m. p. 142° (yield 2 g.) (Found : Cl, 20·3; Te, 36·4. $C_9H_{24}O_2TeCl_2$ requires Cl, 20·1; Te, 36·2%).

4-iso*Butyl*cyclo*telluropentane*-3 : 5-*dione*,

$$(CH_3)_2CH{\cdot}CH_2{\cdot}CH{<}\begin{matrix}CO{\cdot}CH_2\\CO{\cdot}CH_2\end{matrix}{>}Te.$$

—The foregoing dichloride when reduced with aqueous potassium metabisulphite yielded a yellow solid sparingly soluble in water. Recrystallised from benzene, the *telluro*-derivative separated in yellow leaflets, m. p. 150° (Found : C, 38·4; H, 5·0. $C_9H_{14}O_2Te$ requires C, 38·4; H, 5·0%).

2. β-*Phenylpropionylacetone*, $C_6H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_3$.

Ethyl β-phenylpropionate, prepared by boiling 209 g. of β-phenylpropionic acid for 2 hours with 900 c.c. of absolute alcohol containing 30 g. of hydrogen chloride, was fractionated until boiling at 244—245°. The Claisen condensation was carried out with acetone and sodium in calculated quantities and ethyl β-phenylpropionate (3 mols.), the acetone being diluted with six times its volume of dry benzene. After 12 hours, the mixture was heated on the water-bath, cooled, and poured on to ice, the aqueous layer being treated successively with acetic acid and cupric acetate. The precipitate consisted of a mixture of copper β-phenylpropionate and *copper β-phenylpropionylacetone*, which were separated by fractional crystallisation from benzene, the latter compound being the more soluble. When purified, it had a greyish-blue colour and melted at 158° (Found : Cu, 14·4. $C_{24}H_{26}O_4Cu$ requires Cu, 14·4%).

2-*Benzyl*cyclo*telluripentane*-3 : 5-*dione* 1 : 1-*Dichloride*.—Hydrogen chloride was evolved with a slight deposition of tellurium when 5 g. of tellurium tetrachloride, 5·3 g. of β-phenylpropionylacetone, and 40 c.c. of purified chloroform were heated on the water-bath for 2 hours. The solution was concentrated in a vacuum desiccator to a dark brown jelly and stirred with light petroleum, but the semi-solid mass showed no tendency to crystallise and accordingly it was reduced with aqueous potassium metabisulphite, when a

yellow solid separated mixed with tarry matter and tellurium. After extraction with hot alcohol, the golden-yellow filtrate yielded 2-*benzyl*cyclo*telluropentane*-3 : 5-*dione* (V) in small, yellow crystals decomposing at 159° (Found : C, 45·8; H, 3·9; Te, 41·0. $C_{12}H_{12}O_2Te$ requires C, 45·6; H, 3·8; Te, 40·4%).

[With Cyril James Allan Taylor.]

1. Copper duodecoylacetone, prepared by the Claisen condensation from methyl undecyl ketone (Morgan and Holmes, *J. Soc. Chem. Ind.*, 1925, **44**, 108T), was decomposed with sulphuric acid in presence of ether. The free β-diketone obtained from the ethereal layer melted at 31—32° and had the characteristic properties of its series.

2-n-*Decyl*cyclo*telluripentane*-3 : 5-*dione* 1 : 1-*Dichloride* (VII).

(VII.) $C_{10}H_{21}\cdot CH(TeCl_2)\cdot CH_2$ / $OC—CH_2—CO$ $\qquad$ $C_{10}H_{21}\cdot CH(Te)\cdot CH_2$ / $OC—CH_2—CO$ (VIII.)

—Four g. of tellurium tetrachloride and 5 g. (1·5 mols.) of duodecoylacetone were heated in chloroform solution for 3 hours. The dark brown oil obtained on evaporation was extracted repeatedly with petroleum (b. p. 40—60°) to remove unchanged diketone and then left for 1 month in a vacuum desiccator. Crystallisation set in and the solid product was stirred successively with carbon tetrachloride and petroleum. The warm benzene extract of this product was diluted with excess of petroleum, when silvery-white flakes separated (yield 21%) (Found : Cl, 16·4; Te, 29·4. $C_{15}H_{26}O_2Cl_2Te$ requires Cl, 16·3; Te, 29·2%).

2-*n*-Decyl*cyclo*telluripentane-3 : 5-dione 1 : 1-dichloride was readily soluble in cold benzene, chloroform, or acetone, less soluble in carbon tetrachloride, and dissolved only sparingly in petroleum; it melted at 89°.

2-n-*Decyl*cyclo*telluropentane*-3 : 5-*dione* (VIII), obtained by the reduction of the preceding substance with alkali bisulphite, crystallised from aqueous alcohol in pale yellow, woolly masses, m. p. 98—99° (decomp.) (Found : C, 49·1; H, 7·1. $C_{15}H_{26}O_2Te$ requires C, 49·25; H, 7·1%).

This telluropentanedione derivative was readily soluble in cold benzene or alcohol, insoluble in water, but dissolved in dilute aqueous caustic soda, especially on warming; on prolonged boiling, tellurium was deposited.

2. *Tellurium Tetrachloride and* 3-*Phenylpropionylacetone.*

Four g. of tellurium tetrachloride were added to 6·0 g. (2 mols.) of 3-phenylpropionylacetone (*Ber.*, 1925, **58**, 340) in 25 c.c. of chloroform, and the solution was boiled for 1—2 hours. After

evaporating off the solvent, the tarry residue was extracted twice with light petroleum and digested with carbon tetrachloride, and the solution in this solvent concentrated, when crystallisation set in. The product, which was much discoloured, separated from carbon tetrachloride in colourless lamellæ, m. p. 64—68°. It gave the enolic reaction with ferric chloride and was very sensitive to moisture; it did not evolve the earthy odour of an *O*-ethyl β-diketone with cold alkali.

The condensation was varied by changing the proportion of diketone, but the products were similar and contained about 19·4% of chlorine, with C, 27·1; H, 2·6%. These numbers did not correspond with the values calculated for a cyclic dichloride, $X''TeCl_2$, or for di- and tri-chlorides of the type $X'TeCl_3$ and X'_2TeCl_4. The reduction product with alkali bisulphite was unstable. It was therefore evident that the condensation of 3-phenylpropionylacetone with tellurium tetrachloride did not lead to a derivative of the *cyclo*telluripentanedione dichloride series.

[With Richard Eatough Kellett.]

1. 2-*Methyl*cyclo*telluropentane*-3 : 5-*dione Dioxime*,

$$\begin{array}{l} CH_3{\cdot}CH\text{—}Te\text{—}CH_2 \\ NOH{:}C\text{—}CH_2\text{—}C{:}NOH. \end{array}$$

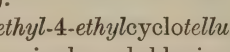
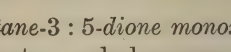
—Two g. of hydroxylamine sulphate in 30 c.c. of water were added to 0·7 g. of 2-methyl*cyclo*telluropentane-3 : 5-dione (J., 1923, **123**, 450) in 50 c.c. of water; the solution was neutralised with sodium hydroxide and warmed on the water-bath. The crude oxime separated, on cooling, in minute, yellow crystals. Extraction of this precipitate with boiling benzene gave a small amount of soluble product, probably monoxime, blackening at 135—150°. The residue dissolved in warm alcohol and separated in greyish-yellow crystals darkening at 153° and melting sharply at 161·5° (Found: N, 10·4; Te, 47·0. $C_6H_{10}O_2N_2Te$ requires N, 10·4; Te, 47·3%).

The dioxime was insoluble in hot water or benzene.

2. *The Oximes of* 2-*Methyl*-4-*ethyl*cyclo*telluropentane*-3 : 5-*dione*. —Two g. of hydroxylamine sulphate in 50 c.c. of water were added to 0·7 g. of 2-methyl-4-ethyl*cyclo*telluropentane-3 : 5-dione (J., 1924, **125**, 758) in 50 c.c. of warm alcohol. Sodium acetate was added with sufficient water to bring the reagents into solution when heated on the water-bath. Some tellurium separated and after 10 minutes the cooled solution deposited a voluminous mass of yellow crystals; the greater part of this dissolved readily in warm benzene, but the nitrogen content of the crystallised product was 7·7, that is, intermediate between 5·0 and 9·4 required for

the mono- and di-oximes respectively. The mixture was extracted with either boiling water or a small amount of benzene. After repeated crystallisation, the more soluble *monoxime* was isolated in bright yellow crystals blackening at 135° and melting at 157° (Found : N, 5·1; Te, 45·1. $C_8H_{13}O_2NTe$ requires N, 5·0; Te, 45·1%).

2-*Methyl*-4-*ethyl*cyclo*telluropentane*-3 : 5-*dione monoxime* (IX) was only sparingly soluble in hot water and decomposed slightly in aqueous solution.

(IX.)   (X.)

2-*Methyl*-4-*ethyl*cyclo*telluropentane*-3 : 5-*dione Dioxime* (X).—Oximation to the dioxime was never complete, even on carrying out the condensation in solutions rendered alkaline with sodium hydroxide, either by direct treatment of the diketone or by the further action of hydroxylamine on the monoxime. The mixed products from either of these operations were extracted with boiling benzene to remove monoxime, and the residues crystallised from boiling alcohol, in which they dissolved without decomposition. The *dioxime* separated as a greyish-yellow, crystalline powder blackening at 170° and decomposing at 182° (Found : N, 9·7; Te, 42·7. $C_8H_{14}O_2N_2Te$ requires N, 9·4; Te, 42·85%).

The dioxime is practically insoluble in hot water or cold benzene, more soluble in the latter on boiling, and dissolves with slight decomposition in warm acetylacetone.

[With Oliver Cecil Elvins.]

1. 4-sec.-*Butyl*cyclo*telluripentane*-3 : 5-*dione Dichloride*.

sec.-Butyl alcohol, synthesised by Wood and Scarf's process (*J. Soc. Chem. Ind.*, 1923, **42**, 13T) (74 g.), was converted into *sec.*-butyl iodide by treating with red phosphorus (20 g.) and iodine (128 g.), the latter reagent being added in small quantities. After warming the mixture, the iodide was distilled off, washed with aqueous sodium carbonate, dried, and fractionated (b. p. 117—118°).

3-sec.-*Butylacetylacetone*, $(CH_3{\cdot}CO)_2CH{\cdot}CH(C_2H_5){\cdot}CH_3$, was obtained by heating in a rotating autoclave at 140—160° for 2 hours (pressure 120 lb. per sq. inch) 35 g. of sodium acetylacetone and 10 g. of *sec.*-butyl iodide. The resulting mixture was filtered, the sodium iodide washed with ether, and the combined filtrates were distilled first under the ordinary and then under reduced pressure. The fraction boiling at 110—113°/13 mm. was again rectified until it ceased to give the red coloration with ferric chloride. The

final product boiled at 109—111°/13 mm., but the yield was only 9% of theory.

3-sec.-*Butylacetylacetone* gave no copper derivative with ammoniacal copper acetate, but underwent condensation with tellurium tetrachloride. A chloroform solution (30 c.c.) of the latter reagent (2·9 g.) and diketone (2·5 g.) evolved hydrogen chloride on boiling and 0·2 g. of tellurium was set free. The filtrate, concentrated in a vacuum to a brown tar, solidified on treatment with light petroleum. The solid product crystallised from benzene in lustrous, colourless, prismatic needles darkening at 162° and melting at 168—169° (yield 37%) (Found: Cl, 20·0. $C_9H_{14}O_2Cl_2Te$ requires Cl, 20·1%).

4-sec.-*Butyl*cyclo*telluripentane*-3 : 5-*dione* 1 : 1-*dichloride* (XI) was reduced with aqueous sodium bisulphite and the insoluble reduction product was extracted with benzene and crystallised from alcohol.

(XI.) CH_2–$TeCl_2$–CH_2 / CO—CH—CO / CH_3·CH·C_2H_5 (XII.) CH_2—Te—CH_2 / CO—CH—CO / CH_3·CH·C_2H_5

4-sec.-*Butyl*cyclo*telluropentane*-3 : 5-*dione* (XII) was obtained in primrose-yellow needles, m. p. 145° (Found: C, 38·2; H, 5·3. $C_9H_{14}O_2Te$ requires C, 38·45; H, 5·0%).

2. 4-sec.-dl-*Amyl*cyclo*telluripentane*-3 : 5-*dione* 1 : 1-*Dichloride*.

(XIII.) CH_2–$TeCl_2$–CH_2 / CO—CH—CO / CH_2·CHMeEt (XIV.) CH_2—Te—CH_2 / CO—CH—CO / CH_2·CHMeEt

—An intimate mixture of 52 g. of *dl*-amyl iodide and 20 g of sodium acetylacetone was maintained at 130° for 2 hours in the rotating autoclave (100 lb. per sq. inch), and finally at 160° for 30 minutes. The oily product and the sodium iodide were treated as in the preceding preparation (p. 2622). dl-sec.-*Amylacetylacetone* was obtained as an oil, b. p. 116°/15 mm. (yield 36%). In alcoholic solution this 3-alkylated diketone developed a purple coloration with ferric chloride, the liquid becoming blue on addition of water. With ammoniacal cupric acetate the *copper* derivative was obtained; it crystallised from methyl alcohol in greenish-grey needles, m. p. 120°, and was very soluble in chloroform, benzene, or petroleum (b. p. 80—100°), but dissolved only slightly in light petroleum (b. p. 40—60°) (Found: Cu, 16·2. $C_{20}H_{34}O_4Cu$ requires Cu, 15·9%).

Condensation of the diketone and tellurium tetrachloride was effected in purified chloroform, and the cyclic dichloride extracted as in the preceding preparation (p. 2623), the yield being 35%.

4-sec.-*Amyl*cyclo*telluripentane*-3 : 5-*dione dichloride* (XIII) crystallised from benzene in colourless, lustrous, prismatic needles darkening at 136° and melting at 162° (Found : Cl, 19·6; Te, 34·5. $C_{10}H_{16}O_2Cl_2Te$ requires Cl, 19·3; Te, 34·8%).

4-sec.-*Amyl*cyclo*telluropentane*-3 : 5-*dione* (XIV), obtained from the preceding dichloride by reduction with bisulphite, crystallised from benzene or dilute alcohol in pale yellow leaflets, dissolving sparingly in hot water and soluble in benzene, but insoluble in petroleum (b. p. 40—60°); m. p. 138—139° (Found : C, 40·9; H, 5·7. $C_{10}H_{16}O_2Te$ requires C, 40·6; H, 5·45%).

Although the two foregoing telluriferous compounds containing *sec.*-amyl groups were obtained as crystalline products, the condensation of tellurium tetrachloride with 3-sec.-*amyldipropionylmethane* resulted in oily products. This 3-alkylated diketone was obtained without using the autoclave by heating under reflux 20 g. of *sec.*-amyl iodide and 5 g. of sodium dipropionylmethane for 1 hour at 140—145°; sodium iodide separated slowly and the oily product on distillation yielded 2·5 g. of the diketone, b. p. 137°/15—17 mm., which developed a purple coloration with ferric chloride.

Copper 3-sec.-*amyldipropionylmethane* was slowly formed on shaking the diketone with ammoniacal cupric acetate. Crystallised from petroleum, b. p. 60—80°, it separated as a greenish-grey meal, m. p. 105°; it was very soluble in benzene or chloroform (Found : Cu, 14·5. $C_{24}H_{40}O_4Cu$ requires Cu, 13·9%).

Addendum.—In addition to the copper derivatives obtained as above from the open-chain diketones, the following metallic derivatives from the cyclic acetylmethyl*cyclo*hexanone (Leser, *Bull. Soc. chim.*, 1900, **23**, 370; 1901, **25**, 196) were examined. The diketone employed had $D_4^{17°}$ 1·024 and $[\alpha]_{5893}^{17°}$ + 105·8°. Its copper derivative was examined for the presence of isomerides by fractional crystallisation from alcohol, but no change in the melting point (186°) was noticed. A benzene solution was too deeply coloured for determination of its rotation.

*Beryllium Acetylmethyl*cyclo*hexanone*, $Be(C_9H_{13}O_2)_2$.—On shaking together a concentrated solution of beryllium acetate containing sodium acetate and 1·5 g. of acetylmethyl*cyclo*hexanone in 30 c.c. of alcohol, a white precipitate of the beryllium derivative was obtained in quantitative yield. This product was very soluble in benzene or chloroform; evaporation of the latter solution led to a glass which became crystalline on rubbing. Minute crystals obtained from petroleum (b. p. 80—100°) melted at 159—160°. Four crops of crystals obtained by fractionation from petroleum were examined at 17° in the polarimeter (0·5 g. in 10 c.c. of benzene; $l = 1$). The rotations and melting points remained constant :

α 2·66°, 2·67°, 2·66°, 2·68°; m. p. 160°, 159·5°, 160°, 159·5°; whence $[\alpha]^{17}_{5893}$ + 106·4° or $[M]$ + 335° (Found: Be, 2·95. $C_{18}H_{26}O_4Be$ requires Be, 3·0%).

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CCCLX.—*Interactions of Tellurium Tetrachloride and Monoketones.*

By GILBERT T. MORGAN and OLIVER CECIL ELVINS.

A COMPREHENSIVE study of the interactions of tellurium tetrachloride and β-diketones summarised in the preceding communication furnishes considerable experimental evidence in support of the view that condensations leading to *cyclo*telluripentanedione dichlorides are due, not to median enolisation of the β-diketones, but to a twofold terminal enolisation of these tautomeric substances. Tellurium tetrachloride combines additively with the two double linkings, a ring structure is set up, and then by loss of hydrogen chloride (2 mols.) the telluripentanedione ring is stabilised, this condensation being characteristic of the majority of known β-diketones (see p. 2612).

If this explanation of the *cyclo*telluripentanedione condensation is correct, then it should be possible to bring about an interaction between tellurium tetrachloride and a monoketone, provided that the latter is capable of enolisation. The general chemistry of the monoketones provides many examples of reactions explicable on the supposition that the immediately effective reagent is a dynamic isomeride produced by enolic change:

$$R{\cdot}CO{\cdot}CH_3 \rightleftharpoons R{\cdot}C(OH){:}CH_2.$$

Our earlier knowledge of organic tellurium derivatives is derived largely from the researches carried out by Michaelis and his pupils in the Rostock laboratories. An investigation dealing *inter alia* with monoketones is due to Rust (*Ber.*, 1897, **30**, 2833), who described the reaction in anhydrous ether between tellurium tetrachloride and acetophenone as leading to *tellurium bisacetophenone dichloride* ("dichlorotelluroacetophenon"), yellowish-white needles,

m. p. 186—187°. We have confirmed this observation except as regards the colour; we cannot substantiate the statement that "Mit gewöhnlichen Aceton gelang es jedoch nicht, ein solches Produkt zu erhalten."

Although the experimental difficulties are greater in the case of acetone than with some of its immediate homologues, nevertheless interaction does occur with the formation of *tellurium bisacetone dichloride*, $(CH_3{\cdot}CO{\cdot}CH_2)_2TeCl_2$. The yield is small—about 17% of theory—due to the comparative instability of the purely aliphatic dichloride and also owing probably to the formation of an even more readily hydrolysable trichloride. The latter supposition is confirmed on passing to the next homologues of acetone, methyl ethyl ketone and diethyl ketone, which furnish, respectively, in excellent yield *tellurium methylethylketone trichloride*, $CH_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}TeCl_3$, and *tellurium diethylketone trichloride*, $CH_3{\cdot}CH_2{\cdot}CO{\cdot}CH(CH_3){\cdot}TeCl_3$.

The lengthening of the normal chain in di-*n*-propyl ketone does not appreciably modify this tendency, for in this case also the sole product is *tellurium di*-n-*propylketone trichloride*,

$$CH_3{\cdot}[CH_2]_2{\cdot}CO{\cdot}CH(C_2H_5){\cdot}TeCl_3.$$

On the other hand, methyl *n*-propyl ketone, methyl *iso*propyl ketone, methyl *n*-butyl ketone, and methyl *iso*butyl ketone resemble acetone itself in furnishing dichlorides (pp. 2628–9).

Accordingly the two modes of reaction may be generalised as follows:

1. $R{\cdot}C(OH){:}CHR' \longrightarrow R{\cdot}C(OH){\cdot}CHR' \longrightarrow R{\cdot}CO{\cdot}CHR'$ (I.)
   $Cl{-}{-}{-}TeCl_3 \qquad Cl \quad TeCl_3 \qquad TeCl_3$

2. $R{\cdot}C(OH){:}CHR' \qquad R{\cdot}CCl(OH){\cdot}CHR'$
   $Cl_2{=}{=}{=}TeCl_2 \longrightarrow TeCl_2 \longrightarrow (R{\cdot}CO{\cdot}CHR')_2TeCl_2.$ (II.)
   $R{\cdot}C(OH){:}CHR' \qquad R{\cdot}CCl(OH){\cdot}CHR'$

The case of pinacolin, or methyl *tert.*-butyl ketone, is noteworthy, for in this instance both products were identified, namely, *tellurium pinacolin trichloride* (III) and *tellurium bispinacolin dichloride* (IV).

(III.) $(CH_3)_3C{\cdot}CO{\cdot}CH_2{\cdot}TeCl_3$ $\qquad$ $\{(CH_3)_3C{\cdot}CO{\cdot}CH_2\}_2TeCl_2$ (IV.)

With pinacolin the enolisation can occur only in one way, whereas in the other foregoing unsymmetrical ketones there are alternative possibilities of enolic change and these complications combined with the hydrolysable nature of the trichlorides have prevented the isolation of both telluriferous products. The respective solubilities of the di- and tri-chloro-derivatives vary irregularly with the

ascent of the homologous series, so that, except in the case of the pinacolin products, only the less soluble compound is isolated.

Moreover, with the substitution of alkyl radicals for the hydrogen atoms of acetone there will be a diminished tendency for enolisation. With the β-diketones this substitution was found to be a determining factor; di*iso*butyrylmethane, $\{(CH_3)_2CH\cdot CO\}_2CH_2$, had lost the property of giving a cyclic tellurium derivative possessed by dibutyrylmethane, $\{CH_3\cdot CH_2\cdot CH_2\cdot CO\}_2CH_2$.

The effect of progressive alkylation of acetone has been tested. Methyl ethyl ketone, diethyl ketone, and methyl *iso*propyl ketone have given characteristic telluriferous derivatives. Two higher homologues, ethyl *iso*propyl ketone and di*iso*propyl ketone, also have been compared. The former undoubtedly reacts with tellurium tetrachloride, for the inorganic reagent passes into solution and hydrogen chloride is evolved. The telluriferous product is, however, oily and readily hydrolysable; so that it was not isolated.

Di*iso*propyl ketone behaves entirely differently from all the other aliphatic ketones examined. Under the same experimental conditions, the tellurium tetrachloride remains undissolved, no hydrogen chloride is evolved, and both reagents may be recovered quantitatively.

Our observations were extended to mixed ketones containing aromatic radicals, and the aliphatic homologues of acetophenone were shown to differ from this substance in yielding *trichlorides*. An exceptionally stable *trichloride* was also obtained from phenyl benzyl ketone.

It is noteworthy that these arylated derivatives, including tellurium bisacetophenone dichloride, are colourless. The yellow tinge of the latter described by Rust may be due to a trace of the yellow etherate of tellurium tetrachloride due to the employment of dry ether as solvent (compare Rohrbaech, *Annalen*, 1901, **315**, 9).

Experimental.

I. *Aliphatic Ketones.*

Tellurium Bisacetone Dichloride, $(CH_3\cdot CO\cdot CH_2)_2TeCl_2$.—Two g. of redistilled acetone (2 mols.) were heated under reflux with 4·7 g. of tellurium tetrachloride (1 mol.) and 30 c.c. of dry chloroform. The turbid yellow solution rapidly evolved hydrogen chloride and after 40 minutes the filtrate from less than 0·1 g. of tellurium was concentrated to a brown syrup in a vacuum desiccator. A small portion was extracted with petroleum (b. p. 40—60°), dissolved in carbon tetrachloride, and the solution diluted with petroleum; crystals then separated which were used for seeding the remainder of the syrup. The resulting crop of colourless needles was drained

on porous plates, when 0·9 g. was obtained, being 16·7% of theory. Recrystallised from carbon tetrachloride and chloroform in equal volumes, the substance separated in colourless, nacreous plates, m. p. 126—128° (Found: C, 22·8; H, 3·35; Te, 40·7; Cl, 22·7. $C_6H_{10}O_2Cl_2Te$ requires C, 23·0; H, 3·2; Te, 40·8; Cl, 22·7%).

Tellurium bisacetone dichloride also separated from chloroform and light petroleum in colourless crystals, a small amount of tellurium being eliminated. When reduced with aqueous bisulphite, the compound was decomposed with separation of tellurium.

Tellurium Methylethylketone Trichloride, $C_2H_5{\cdot}CO{\cdot}CH_2{\cdot}TeCl_3$.—The boiling turbid yellow solution of 4 g. of tellurium tetrachloride, 1·9 g. of methyl ethyl ketone, and 28 c.c. of dry chloroform rapidly evolved hydrogen chloride and only a trace of tellurium separated. On concentration the brown syrup yielded 3·5 g. of *trichloride* (75% of theory), which crystallised from carbon tetrachloride in small, colourless, prismatic needles, m. p. 101—101·5° (Found: Cl, 34·7; Te, 42·35. $C_4H_7OCl_3Te$ requires Cl, 34·9; Te, 41·8%). The trichloride was readily soluble in chloroform; it decomposed slightly in boiling solvents and blackened on keeping.

Tellurium Bismethyl-n-*propylketone Dichloride*,

$$(C_3H_7{\cdot}CO{\cdot}CH_2)_2TeCl_2.$$

—The yellow solution from 3 g. of methyl *n*-propyl ketone (b. p. 101·5—102°), 4·1 g. of tellurium tetrachloride, and 25 c.c. of chloroform, when decanted from tellurium (0·2 g.) and concentrated to a syrup, did not solidify until triturated with petroleum; colourless needles then separated (0·8 g.). As this substance decomposed in contact with its mother-liquor, it was rapidly dried on porous tile and recrystallised from carbon tetrachloride; m. p. 92—93° (Found: Cl, 19·5; Te, 34·3. $C_{10}H_{18}O_2Cl_2Te$ requires Cl, 19·3; Te, 34·6%).

*Tellurium Bismethyl*iso*propylketone Dichloride*,

$$\{(CH_3)_2CH{\cdot}CO{\cdot}CH_2\}_2TeCl_2.$$

—Methyl *iso*propyl ketone (3 g.), 4·1 g. of tellurium tetrachloride, and 28 c.c. of chloroform rapidly evolved hydrogen chloride and the concentrated solution yielded 3·4 g. of crystalline product (52% of theory). The *dichloride* crystallised readily from carbon tetrachloride in colourless needles softening at 85° and melting at 90° (Found: Cl, 19·4; Te, 34·3. $C_{10}H_{18}O_2Cl_2Te$ requires Cl = 19·3; Te = 34·6%).

Tellurium Bismethyl-n-*butylketone Dichloride*,

$$(C_4H_9{\cdot}CO{\cdot}CH_2)_2TeCl_2.$$

—Methyl *n*-butyl ketone (3 g.), 2·7 g. of tellurium tetrachloride, and 20 c.c. of chloroform were treated as in the preceding preparation. The brown syrup yielded no solid product until extracted with

petroleum to remove unchanged ketone. This extract yielded a small amount of solid, and a further amount was obtained by extracting the residual oil with carbon tetrachloride (total yield 1·1 g.). After two crystallisations from this solvent, nacreous, colourless plates were obtained, m. p. 62° (Found: Cl, 17·8. $C_{12}H_{22}O_2Cl_2Te$ requires Cl, 17·9%).

Tellurium Bismethylisobutylketone Dichloride,

$$\{(CH_3)_2CH\cdot CH_2\cdot CO\cdot CH_2\}_2TeCl_2.$$

—The addition of 3·6 g. of tellurium tetrachloride to 3 g. of methyl *iso*butyl ketone in 20 c.c. of chloroform resulted in a bulky, yellow precipitate, which decomposed rapidly on exposure to the atmosphere. On heating the mixture under reflux, this precipitate dissolved with evolution of hydrogen chloride, and the clear brown solution on concentration yielded 2·7 g. of colourless needles (45·5% of theory). Recrystallised from carbon tetrachloride, the substance separated in colourless plates, m. p. 95°; the acicular form gave the same mixed melting point (Found: Cl, 17·8; Te, 31·75. $C_{12}H_{22}O_2Cl_2Te$ requires Cl, 17·9; Te, 32·2%).

Tellurium Diethylketone Trichloride, $CH_3\cdot CH_2\cdot CO\cdot CH(CH_3)\cdot TeCl_3$. —Less than 0·1 g. of tellurium was eliminated on boiling together 2 g. of diethyl ketone, 3·1 g. of tellurium tetrachloride, and 22 c.c. of dry chloroform; the filtrate on concentration yielded several crops of trichloride (3·1 g. or 84·6% of theory). Recrystallised from carbon tetrachloride, the *trichloride* separated in colourless plates, m. p. 77—78° (Found: Cl, 33·4; Te, 40·5. $C_5H_9OCl_3Te$ requires Cl, 33·5; Te, 40·0%). The trichloride decomposed slightly in hot solvents.

*Tellurium Di-*n*-propylketone Trichloride*,

$$CH_3\cdot CH_2\cdot CH_2\cdot CO\cdot CH(CH_2\cdot CH_3)\cdot TeCl_3.$$

—The concentrated solution from 3 g. of tellurium tetrachloride, 1·3 g. of butyrone, and 20 c.c. of chloroform deposited masses of greyish-brown, silky needles (3 g. or 77% of theory). Recrystallised from carbon tetrachloride and petroleum, the *trichloride* was obtained in colourless needles, m. p. 70° (Found: Cl, 30·7; Te, 37·1. $C_7H_{13}OCl_3Te$ requires Cl, 30·7; Te, 36·7%).

This trichloride was somewhat unstable in hot acetone and underwent hydrolysis on exposure to moist air.

Interactions of Tellurium Tetrachloride and Pinacolin.—The turbid yellow solution of 2·5 g. of pinacolin, 3·4 g. of tellurium tetrachloride, and 25 c.c. of chloroform evolved hydrogen chloride on boiling and after 40 minutes the brown liquid, when treated with half its bulk of petroleum (b. p. 40—60°), yielded *tellurium pinacolin trichloride* (formula III) in colourless plates. When this was recrystallised from carbon tetrachloride, some elimination of tellurium

occurred in the hot solvent; the filtrate deposited colourless, rhomboidal platelets softening at 110° and melting at 114—115°. The yield was 0·9 g. or 21% of theory (Found: Cl, 32·0; Te, 38·1. $C_6H_{11}OCl_3Te$ requires Cl, 32·0; Te, 38·3%).

The mother-liquor from the trichloride preparation furnished on concentration a crystalline residue which after two crystallisations from carbon tetrachloride separated in colourless needles, m. p. 191—192°; yield 1·6 g. or 26% of theory (Found: C, 36·0; H, 5·7; Cl, 18·25; Te, 32·3. $C_{12}H_{22}O_2Cl_2Te$ requires C, 36·3; H, 5·55; Cl, 17·9; Te, 32·2%).

Tellurium bispinacolin dichloride (formula IV) was much more permanent in air than the preceding trichloride, but all attempts at removing the chlorine were unsuccessful; the use of potassium metabisulphite or neutral sodium sulphite (Vernon, J., 1920, **117**, 892) led to elimination of tellurium.

Interaction of Tellurium Tetrachloride and Ethyl iso*Propyl Ketone.*—Fifteen g. of diethyl ketone were alkylated with methyl iodide and caustic potash at 120—130° (Nef, *Annalen*, 1900, **310**, 325). The product was fractionated and ethyl *iso*propyl ketone boiling at 114—116° was employed in the following condensations. Tellurium tetrachloride (2·7 g.) was readily dissolved by boiling in 20 c.c. of dry chloroform containing from 1 to 2 g. of the ketone. Hydrogen chloride was evolved, only a small amount of tellurium (0·1 g.) was eliminated, and on concentration a brown syrup was obtained which did not, however, yield a crystalline product. Extraction with organic solvents and the addition of hydrogen bromide or ferric chloride also failed to furnish solid derivatives. On exposure to air the oily syrup slowly evolved hydrogen chloride, and the final residue contained only inorganic compounds of tellurium.

*Tellurium Tetrachloride and Di*iso*propyl Ketone.*—Di*iso*propyl ketone, b. p. 123—124°, was prepared by Nef's method (*loc. cit.*) from ethyl *iso*propyl ketone and purified through its crystalline oxime (m. p. 28°), which was distilled under reduced pressure and hydrolysed with concentrated hydrochloric acid. Tellurium tetrachloride (2·5 g.) was boiled for an hour with 2 g. of di*iso*propyl ketone and 20 c.c. of dry chloroform, a process which in all the preceding experiments had led to condensation. In this case, however, the tellurium tetrachloride remained insoluble and unchanged.

II. *Mixed Ketones containing Aromatic Radicals.*

Tellurium bisacetophenone dichloride, prepared by Rust (*loc. cit.*) by heating 2 mols. of acetophenone with 1 mol. of tellurium

tetrachloride in dry ether, was then described as crystallising in yellow needles, m. p. 186—187°.

Three g. of acetophenone, 3·5 g. of tellurium tetrachloride, and 15 c.c. of chloroform were boiled under reflux and the dark brown solution was concentrated to a crystalline mass of dichloride. After two crystallisations from chloroform, tellurium bisacetophenone dichloride separated in colourless needles, m. p. 186—187° (Found: Cl, 16·2. Calc., Cl, 16·3%). Reduction of this dichloride with potassium metabisulphite led to the elimination of tellurium.

Tellurium Phenylethylketone Trichloride,

$$C_6H_5\cdot CO\cdot CH(CH_3)\cdot TeCl_3.$$

—After boiling for 45 minutes, the solution of 3 g. of tellurium tetrachloride, 3 g. of phenyl ethyl ketone, and 25 c.c. of chloroform was concentrated to the crystallising point. The solid (2·5 g. or 61% of theory) was crystallised from carbon tetrachloride in a dry atmosphere to obviate hydrolytic decomposition by moisture, when large, colourless, rhomboidal prisms separated, m. p. 114—115° (Found: C, 29·1; H, 2·5; Cl, 29·0; Te, 35·0. $C_9H_9OCl_3Te$ requires C, 29·4; H, 2·45; Cl, 29·0; Te, 34·7%).

*Tellurium Phenyl-*n*-propylketone Trichloride*,

$$C_6H_5\cdot CO\cdot CH(CH_2\cdot CH_3)\cdot TeCl_3.$$

—The condensation of 2·8 g. of tellurium tetrachloride and 3 g. of phenyl *n*-propyl ketone in 20 c.c. of chloroform was carried out as in the preceding preparation. On concentration, 2·8 g. of solid were obtained (71% of theory). Recrystallised from carbon tetrachloride, the product separated in colourless prisms blackening at 122° and melting at 128—129° (Found: Cl, 27·7; Te, 33·1. $C_{10}H_{11}OCl_3Te$ requires Cl, 27·95; Te, 33·5%).

Tellurium Phenylbenzylketone Trichloride,

$$C_6H_5\cdot CO\cdot CH(C_6H_5)\cdot TeCl_3.$$

—Phenyl benzyl ketone was prepared by reduction of benzoin with zinc dust and glacial acetic acid (Sudborough, J., 1897, **71**, 219). Two g. were condensed with 2·7 g. of tellurium tetrachloride in 20 c.c. of chloroform. The concentrated solution furnished a greyish-green, crystalline mass (2·6 g. or 60% of theory), which was recrystallised from carbon tetrachloride or from chloroform–petroleum, when colourless, facetted prisms were obtained, m. p. 142—143° (Found: Cl, 24·7; Te, 30·1. $C_{14}H_{11}OCl_3Te$ requires Cl, 24·8; Te, 29·7%).

This trichloride was readily reduced by aqueous potassium metabisulphite to a yellow solid, which, however, was very unstable and decomposed rapidly either on exposure or in chloroform solution.

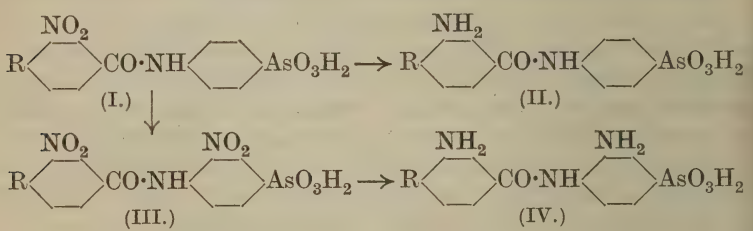
The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research and to the Government Grant Committee of the Royal Society for grants which have helped to defray the expense of this investigation.

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EDGBASTON. [*Received, October 2nd,* 1925.]

CCCLXI.—*Trypanocidal Action and Chemical Constitution. Part II. Arylamides of 4-Aminophenylarsinic Acid.*

By HAROLD KING and WILLIAM OWEN MURCH.

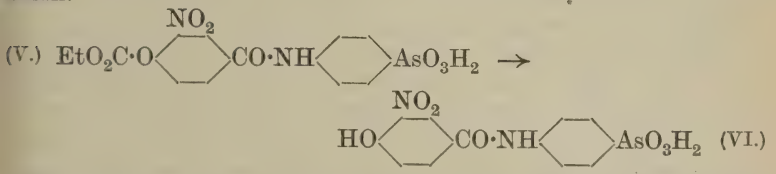
IN Part I (J., 1924, **125**, 2595), about 25 arylamides of 4-aminophenylarsinic acid were described with their toxicities to mice and their curative action on experimental trypanosomiasis in mice. Of this series of substances, the one clearly indicated for further development was 3′-aminobenzoyl-4-aminophenylarsinic acid (II; R = H), which had a toxicity of 0·6 and a temporary curative action in a dose of 0·18 milligram per gram of mouse.



There were two obvious ways of modifying this structure with a view to following the change in its curative action. The one was to replace the *m*-aminobenzoyl group by other *m*-aminobenzoyl radicals substituted in the *p*-position. The parent *p*-substituted *m*-nitrobenzoic acids are readily accessible in quantity, provided the *p*-substituent is *op*-directive, by starting from the *p*-substituted anilines, which by the Sandmeyer reaction for the preparation of nitriles, saponification, and nitration yield the required *p*-substituted *m*-nitrobenzoic acids. Anisic acid is, however, more readily accessible from anethole, $MeO{\cdot}C_6H_4{\cdot}CH{:}CHMe$, a process having been evolved whereby it may be obtained in large quantities in almost quantitative yield.

The other way was to re-nitrate the mononitroarylamide (I) in the hope that the main product would be a dinitroarylamide of the type (III), which would give a series of interesting diamines (IV).

This has now been done, a series of *p*-substituted *m*-nitrobenzoic acids having been prepared in which R = Me, OMe, OEt, O·CO_2Et, or Cl. These readily yield the corresponding acid chlorides, which can be introduced into 4-aminophenylarsinic acid in 40—80% yield by suitable modifications of the Schotten-Baumann method, *ethylcarbonatonitrobenzoyl chloride*, for instance, being relatively sensitive to hydroxyl ions, necessitating the use of sodium acetate as halogen acid fixative. The corresponding aminoarsinic acids were obtained by reduction with ferrous chloride and alkali in 55—95% yield, the *ethylcarbonatonitrobenzoyl-4-aminophenylarsinic acid* (V) being first converted into the *hydroxynitro-acid* (VI) by alkali.



The maximum dose tolerated by mice, expressed in milligrams per gram of mouse, of the six isomeric *nitro*-benzoylarsinic acids (I) with variation of the group R is shown below :

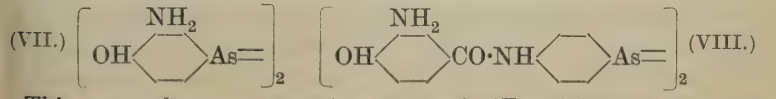
R = ...	H.	Me.	OMe.	OEt.	OH.	Cl.
Dosis tolerata	0·6	0·2	0·2	0·2	0·8	0·2

whereas for the corresponding *amino*-acids (II) the maximum tolerated dose and the minimum curative dose on *Trypanosoma equiperdum* in mice are given,

R = ...	H.	Me.	OMe.	OEt.	OH.	Cl.
Dosis tolerata	0·6	0·3	0·7	0·6	0·5	0·1
Dosis curativa	0·18	0·15	0·4	0·6	0·2	0·075
	(r = 3)	(r = 10)		(r = 10)	(r = 7)	

r signifying the number of days during which the blood-stream remains free from trypanosomes. Of this group, two members have effected permanent cures in mice and of these two the *p*-methoxy-derivative was superior to the *p*-chloro-derivative.

Aminohydroxybenzoyl-4-aminophenylarsinic acid, the reduction product of (VI), was of special interest because it contained the *o*-aminophenol grouping of salvarsan (VII) and could therefore be reduced to an *arseno*-derivative (VIII), soluble in alkalis and suitable for experimental testing on trypanosomiasis.

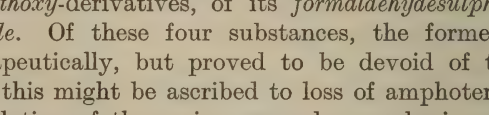


This arseno-base was ten times as toxic (T = 0·05) as its parent amino-acid and on two-fifths of this dose (C = 0·02) a temporary

cure of mice was effected for 7 days. The therapeutic indices, C/T, for the parent amino-acid and its arseno-derivative are thus identical. Both are far inferior to salvarsan.

The acetylation of the amino-groups in substituted arsinic acids can readily be effected by dissolving in alkali and shaking with excess of acetic anhydride. When applied to the *o*-aminophenol grouping in 3′-amino-4′-hydroxybenzoyl-4-aminophenylarsinic acid, a practically quantitative yield was obtained of the ON-*diacetyl* derivative, which, on standing in solution in *N*-sodium hydroxide, gave the N-*acetyl* derivative. *ON*-Diacetylation under such conditions has apparently only once previously been observed, by Raiford and Greider (*J. Amer. Chem. Soc.*, 1924, **46**, 430), who obtained some diacetyl derivative on acetylation of *o*-aminophenol in sodium hydroxide solution, it having been overlooked by Lumière and Barbier (*Bull. Soc. chim.*, 1905, **33**, 783), who recommended aqueous acetylation. It seems, however, to be a general method for the preparation of *ON*-diacetyl derivatives, provided the product, when once it is formed, is never subjected to high concentrations of hydroxyl ions. Applied to *o*-aminophenol-*p*-arsinic acid, it readily yields the *ON*-diacetyl derivative. 3′-*Acetylamino*-4′-*acetoxybenzoyl*-4-*aminophenylarsinic acid* proved to be devoid of trypanocidal action.

The avenue opened by the curative action of *aminoanisoylaminophenylarsinic acid* was explored by the preparation of its N-*acetyl* and N-*carbethoxy*-derivatives, of its *formaldehydesulphoxylate* and its *carbamide*. Of these four substances, the former two were tested therapeutically, but proved to be devoid of trypanocidal action. As this might be ascribed to loss of amphoteric character through acylation of the amino-group by non-basic radicals, two, more complex, tri-nuclear amides were prepared, namely, the 3″-*aminobenzoyl*-(R = H) and 3″-*amino*-4″-*anisoyl*-(R = OMe) derivatives of 3′-amino-4′-anisoyl-4-aminophenylarsinic acid (IX) in which amphoteric character was preserved. These also were devoid of trypanocidal action.



(IX.)

The nitration of a series of *p*-substituted benzoic acids in which the *p*-substituent is Me, OMe, OEt, O·CO_2Et, or Cl has enabled us to effect both a comparison of the relative ease of nitration of these benzoic acids and the relative ease of replacement of the carboxyl group by the nitro-group during nitration. The first

three acids are readily nitrated on the water-bath by 70% nitric acid; the last two are unaffected by acid of this strength, but are nitrated in 76 and 90% yield, respectively, by 94% nitric acid. If other comparable observations from the literature be included, the following series is obtained:

HNO_3 %	14—30%.	70%.	92—94%.
R = ...	OH,[1]NMe_2[2].	Me,OMe,OEt.	F,[3]Br,[4]Cl,O·CO_2Et.

(1) Griess, *Ber.*, 1887, **20**, 408. (2) Reverdin, *Ber.*, 1907, **40**, 2442. (3) Rouche, *Bull. Acad. roy. Belg.*, 1921, 534. (4) Hübner, Philipp, and Ohly, *Annalen*, 1867, **143**, 248.

This series is substantially the one to be expected from a consideration of the relative directive powers of a member of any one of these groups in competition with a member to the right of it, for nitric acid, the two substituents being situated in the para- or ortho-positions with respect to each other. Thus there is ample evidence in the literature that when either OH or NMe_2 is set against Me, OMe, OEt, F, Cl, Br in the para-position, the NO_2 group enters mainly ortho to OH or NMe_2; when the two groups are in the ortho-position to each other, the evidence, although not so complete, supports the same conclusion. Again, when MeO or EtO is set against Cl or Br in the para- or ortho-position, the NO_2-group is preferentially directed ortho or para respectively to the MeO or EtO group in both cases, but, in the relative directive powers of Me and halogens there is an element of doubt.* In 1912, Holleman and Wibaut (*Proc. K. Akad. Wetensch. Amsterdam*, **15**, 594), from the nitration of *o*-, *m*-, and *p*-chlorotoluenes, drew the conclusion that chlorine induces a velocity of substitution 1·5 times as great as that caused by the methyl radical. Later, however, Holleman (*Rec. trav. chim.*, 1915, **34**, 283) found that in the nitration of *p*-bromotoluene the methyl group had undoubtedly the superior orienting power. The latter result is more in accord with our own observations. We have been unable to find in the literature anything bearing on the relative orienting influence of the O·CO_2Et group on an entering nitro-group. The relative directive powers for ortho-substitution of a nitro-group may therefore be written in the order OH,NMe_2 > Me,OMe,OEt > F,Cl,Br,O·CO_2Et.

In every case during nitration partial replacement of the carboxyl group by the nitro-group takes place with formation of *p*-substituted nitrobenzenes and is evidently a general phenomenon. This is contrary to the view of Rouche (*loc. cit.*), who claimed that there was no formation of chloro- or bromo-nitrobenzenes by nitration of the chloro- or bromo-benzoic acids. In addition,

* This is confirmed by the recent work of Francis, Hill, and Johnston (*J. Amer. Chem. Soc.*, 1925, **47**, 2231).

further nitration to 2 : 4-dinitro-derivatives takes place to some extent depending on the time of heating. The relative yields of non-acidic fractions obtained on pouring the nitration mixtures into water are shown below.

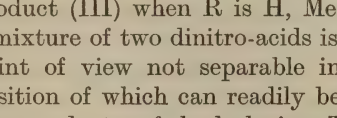
R = ...	Cl.	Me.	F.[1]	OMe.	OEt.	O·CO_2Et
Yield %	1·1	2	11	11·5	14	15·5
HNO_3 %	94	70	92	70	70	94
Time of heating ...	10	30	120	30	10	10 mins.

[1] Rouche *loc. cit.*

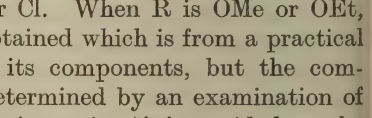
Owing to the variation in strength of nitric acid used and the time of heating, the only deductions allowable are that *O*-substituents and possibly fluorine greatly facilitate replacement of CO_2H by NO_2, and that O·CO_2Et has a different relative orienting power to para-substitution from that which it has to ortho-substitution. It would be of interest to know whether the accumulation of groups in 3 : 4 : 5-trimethyl-, trichloro-, or trifluoro-benzoic acids would enhance the ease of replacement of CO_2H by NO_2 just as accumulation of the MeO results in increased displacement of the formyl (Salway, J., 1909, **95**, 1155) or carboxyl (Harding, J., 1911, **99**, 1585) grouping. The sulpho-group also is replaced to the extent of 5% by the nitro-group during the nitration of *p*-toluenesulphonic acid, as will be shown in a future communication.

For the saponification of *p*-toluonitrile, Herb (*Annalen*, 1890, **258**, 10) recommended the use of 75% sulphuric acid. When applied to *p*-ethoxybenzonitrile, EtO·C_6H_4·CN, this had an unexpected result, phenol-*p*-sulphonic acid, OH·C_6H_4·SO_3H, being formed in good yield and no trace of the required carboxylic acid. A weaker sulphuric acid (60%), however, yielded the required acid and amide in satisfactory yield.

The dinitration of this series of mononitroarylamides (I) proceeds smoothly, but, as might be anticipated, only yields exclusively one product (III) when R is H, Me, or Cl. When R is OMe or OEt, a mixture of two dinitro-acids is obtained which is from a practical point of view not separable into its components, but the composition of which can readily be determined by an examination of the products of hydrolysis. The isomeric *dinitro*-acid has the structure (X), and the two arsinic acids obtained on hydrolysis of this and its isomeride (III) are almost quantitatively separable



(III.)



(X.)

by 0·5*N*-hydrochloric acid. By this means it has been shown that whereas in the cases where R = H, Me, or Cl, the second

NO_2-group enters a different nucleus from the one in which the NO_2-group is already present, when R = OMe or OEt, the NO_2-group is distributed between the two nuclei in the ratios 3 : 7 and 3 : 5, respectively, in favour of the nucleus without a NO_2-group. The *diamines* (IV) were obtained on reduction with ferrous chloride and alkali.

The toxicities and curative action of the dinitro- and diamino-arsinic acids, where determined, are given below :

	Dinitro-acids.			*Diamino-acids.*		
R = ...	H.	Me.	Cl.	H.	Me.	Cl.
Dosis tolerata	0·1	0·025	0·2	>3·5	1·0	1·25
Dosis curativa	0·06	—	—	2	0·75	0·5
	(r = 2)					(r = 29)

Comparison of this table with the previous one for the mono-amino-acids shows that the introduction of a second amino-group lowers the toxicity many-fold, and at the same time the substances acquire permanent curative properties. It is of interest that 3 : 3′-dinitrobenzoyl-4-aminophenylarsinic acid causes a temporary disappearance of trypanosomes from the blood-stream for 2 days. The isomeric 3′ : 5′-dinitrobenzoyl-4-aminophenylarsinic acid was prepared, but attempts to isolate the arsinic acid containing the *m*-phenylenediamine group from it by reduction were unsuccessful.

We desire to acknowledge our indebtedness to Miss F. M. Durham and Miss J. Marchal of this department for the painstaking care with which they have determined the toxicities and trypanocidal action of the compounds described in this paper.

Experimental.

3 : 3′-*Dinitrobenzoyl*-4-*aminophenylarsinic Acid* (III; R = H).—Benzoyl-*p*-aminophenylarsinic acid (19·3 g.) dissolved in 45 c.c. of sulphuric acid was nitrated at 0° by addition of a mixture of 8·5 c.c. of nitric acid (d 1·4) and 11·4 c.c. of sulphuric acid. The crude product obtained by pouring on to ice was collected, allowed to air-dry, and digested on the water-bath with 100 c.c. of glacial acetic acid. The product was now crystalline and the filtrate could be used for subsequent batches. The yield was 92% of the theoretical. This *acid* crystallised from 170 parts of boiling glacial acetic acid in fine, silky needles, forming a *monohydrate* (Found : Loss at 100°, 5·1, 5·0. $1H_2O$ requires loss, 4·2%. Found : As, 18·1. $C_{13}H_{10}O_8N_3As$ requires As, 18·2%). With alkali (1 mol.), it forms sparingly soluble *sodium* and *potassium* salts.

Hydrolysis of 3 : 3′-*Dinitrobenzoyl*-4-*aminophenylarsinic Acid*.—(a) *With acid*. When the dinitro-acid (8·2 g.) was boiled for 2 hours

with 100 c.c. of 16% hydrochloric acid, it was recovered mainly unchanged (6·4 g.). The other products isolated were a small quantity of *o*-nitroaniline, *m*-nitrobenzoic acid, and 3-nitro-4-aminophenylarsinic acid.

(b) *With alkali.* The dinitro-acid (6·3 g.) was boiled for 2 hours with 100 c.c. of *N*-sodium hydroxide. Practically quantitative yields were obtained of *m*-nitrobenzoic acid and 3-nitro-4-aminophenylarsinic acid. There was no *o*-nitroaniline found.

3 : 3′-*Diaminobenzoyl*-4-*aminophenylarsinic Acid* (IV; R = H).—The dinitro-acid (16·4 g.) was dissolved at — 5° in 292 c.c. of 2*N*-sodium hydroxide and treated with 101 g. (10% excess) of ferrous chloride dissolved in 124 c.c. of water. To the mixture 292 c.c. of 2*N*-sodium hydroxide were added, the temperature throughout being below 0°. The ferric hydroxide was filtered off and extracted three times by thorough mixing with 600 c.c. of 0·2*N*-sodium hydroxide each time. The combined filtrates were made neutral to Congo-paper and after keeping for 24 hours at 0° the separated diamino-acid was collected. The filtrate was made alkaline with concentrated ammonia, treated with 50 c.c. of magnesium chloride solution (1 : 1), and heated for 30 minutes in the boiling-water bath. The precipitated magnesium salt was collected, dissolved whilst still damp in *N*-hydrochloric acid, and the acidity to Congo-paper removed by addition of saturated sodium acetate solution. The diamino-acid crystallised readily (total yield was 7·8 g. or 56%). The *diamino*-acid so prepared crystallises in clusters of leaflets. It diazotises and couples with alkaline β-naphthol with production of a deep red colour (Found: As, 20·9. $C_{13}H_{14}O_4N_3As$ requires As, 21·3%).

3 : 5-*Dinitrobenzoic Acid.*—The following process is an improvement on that of Shukov (*Ber.*, 1895, **28**, 1800).

Ten g. of fused benzoic acid were dissolved in 100 g. of sulphuric acid and treated with 18·2 c.c. of fuming nitric acid. The solution was heated on the water-bath for 10 hours and poured into a litre of ice and water. The product (10 g.), m. p. 202°, was washed with a little hot water and reprecipitated from dilute ammonia. It then melted at 203—204°.

3′ : 5′-*Dinitrobenzoyl*-4-*aminophenylarsinic Acid* (X; R = H).—Sodium *p*-aminophenylarsinate pentahydrate (25—26 g.) dissolved in 320 c.c. of 5% sodium hydroxide and cooled to — 3° was treated with 40 g. (2 mols.) of 3 : 5-dinitrobenzoyl chloride dissolved in toluene. The mixture was stirred for 45 minutes after all the acid chloride had been added. After acidification, the mixture of acids was collected, dried, and extracted with ether. The insoluble arsinic acid was reprecipitated from ammoniacal solution (yield

84%). This *dinitro-arsinic acid* crystallises from 80 parts of boiling 90% formic acid in fine needles. In glacial acetic acid it is much less soluble (Found : As, 18·3. $C_{13}H_{10}O_8N_3As$ requires As, 18·2%). The maximum tolerated dose for mice is 0·5 mg. per g. of mouse. Attempts to obtain the diamino-arsinic acid by reduction in alkaline solution with ferrous chloride were unsuccessful.

2-*Nitro*-p-*toluic Acid*.—This acid was prepared by the following process, which is an improvement on that of Fittig and Ramsay (*Annalen*, 1873, **168**, 251). *p*-Toluic acid (20 g.) was suspended in 200 c.c. of nitric acid (*d* 1·4) and heated on the water-bath for 30 minutes. On pouring into water, the yield of nitro-acid was 23·5 g., m. p. 186—187°. By ether extraction of the acid in alkaline solution, 0·4 g., and of its aqueous mother-liquor, 0·6 g., of crude *p*-nitrotoluene were obtained, m. p. 51°.

2-*Nitro*-p-*toluoyl chloride*, prepared by the action of phosphorus pentachloride, boils at 167—168° (corr.)/16 mm. and melts at 20—21° (corr.). This acid chloride has recently been described as an oil (Johnson and Soderman, *J. Amer. Chem. Soc.*, 1925, **47**, 1392).

3′-*Nitro*-4′-*toluoyl*-4-*aminophenylarsinic Acid* (I; R = Me).—This acid was prepared in the same way as *p*′-nitrobenzoyl-*p*-aminophenylarsinic acid (J., 1924, **125**, 2602). The acid chloride, however, reacts so slowly that stirring has to be continued for 2 or 3 hours. The mixed acids obtained on acidification were dried and extracted with ether in a Soxhlet apparatus (yield 55%).

This arsinic acid is sparingly soluble in boiling acetic or formic acid and crystallises in small needles (Found : As, 19·6. $C_{13}H_{13}O_6N_2As$ requires As, 19·7%).

3′-*Amino*-4′-*toluoyl*-4-*aminophenylarsinic Acid* (II; R = Me).—3′-Nitrotoluoyl-4-aminophenylarsinic acid (11·4 g.) was dissolved in 110 c.c. of chilled 2*N*-sodium hydroxide and 40 g. of ferrous chloride (20% excess) in 50 c.c. of water were run in, the temperature being maintained between 0° and − 5°. Finally, 130 c.c. of 2*N*-sodium hydroxide were added. The ferric hydroxide was filtered off and extracted with two successive portions each of 240 c.c. of 0·4*N*-sodium hydroxide. The combined filtrates were neutralised to Congo-paper, and the crude acids collected. These were warmed with successive portions of *N*-hydrochloric acid at 50° until no diazotisable material was left. On addition of saturated sodium acetate solution to the successive filtrates, the aminoarsinic acid was precipitated in fan-shaped clusters of small, white needles. A further small quantity can be isolated from the first precipitation mother-liquors by addition of ammonia and magnesium chloride and heating the solution. The magnesium salt separates

readily, is dissolved in excess of *N*-hydrochloric acid, and the free acid precipitated by sodium acetate. The yield was 5·7 g. or 54% of the theoretical.

This amino-arsinic acid is very sparingly soluble in cold 3*N*-mineral acids, but dissolves readily on warming. The *hydrochloride* crystallises in small needles, the *nitrate* in minute needles, and the *sulphate* in square plates. It diazotises and couples with alkaline β-naphthol with production of a blood-red colour (Found: As, 21·2. $C_{14}H_{15}O_4N_2As$ requires As, 21·4%).

3 : 3′-*Dinitro*-4′-*toluoyl*-4-*aminophenylarsinic Acid* (III; R = Me).—The mononitro-acid (7·5 g.) dissolved in sulphuric acid (20 c.c.) was nitrated at 0° with a mixture of 1·9 c.c. of sulphuric acid and 1·4 c.c. of nitric acid (*d* 1·4). The yellow solid obtained on pouring on to ice was collected and when digested on the water-bath with glacial acetic acid became crystalline (yield 8 g.). This *dinitro-acid* is sparingly soluble in boiling acetic or formic acid and crystallises in needles (Found: As, 17·7. $C_{14}H_{12}O_8N_3As$ requires As, 17·6%).

Hydrolysis of 3 : 3′-*Dinitro*-4′-*toluoyl*-4-*aminophenylarsinic Acid.*—Two g. of the acid were boiled for 2 hours with 30 c.c. of *N*-sodium hydroxide. The acids obtained (2·05 g.) on neutralisation to Congo-paper were extracted in a Soxhlet apparatus with ether. The ether-soluble portion (0·8 g.) consisted of pure 2-nitro-*p*-toluic acid, and the ether-insoluble portion of 3-nitro-4-aminophenylarsinic acid (1·25 g.), the yields being practically quantitative.

3 : 3′-*Diamino*-4′-*toluoyl*-4-*aminophenylarsinic Acid* (IV; R = Me).—The dinitro-acid (8·5 g.) was reduced in the way described for the acid without the methyl group (above), save that it was found advantageous to increase the excess of ferrous chloride used from 10% to 20%, and with it the amount of alkali to secure faint alkalinity at the end of the reduction. The alkaline filtrates from the ferric hydroxide extraction, on neutralisation to Congo-paper, gave no precipitate of diamino-acid. The acid was, however, precipitated as the magnesium salt in ammoniacal solution by heating on the water-bath. The magnesium salt was dissolved in 70 c.c. of *N*-hydrochloric acid, and the *diamino-acid* liberated by addition of saturated sodium acetate solution (yield 4·2 g. or 57%).

This diamino-arsinic acid separates, when liberated as described above, in sphæro-crystals (Found: As, 20·4. $C_{14}H_{16}O_4N_3As$ requires As, 20·5%). Diazotised with sodium nitrite in hydrochloric acid solution, it turns yellow and couples intensely with alkaline β-naphthol with production of a brownish-red colour.

Preparation of Anisic Acid.—Pure crystalline anethole (11·1 g.) was stirred vigorously with 50 c.c. of water at room temperature, and 34·4 g. of potassium permanganate in 1075 c.c. of water were

added at a constant rate within 75 minutes. No attempt was made to regulate the temperature, which at its maximum was below 35°. The very slight excess of permanganate was reduced by warming with alcohol. After filtration, and extraction of the manganese oxides with dilute alkali, the combined filtrates gave, on acidification, 9·0 g. of almost pure anisic acid. An aliquot portion of the filtrate extracted with ether indicated the presence of a further 1·5 g. of equally pure anisic acid. The total yield is about 92% of the theoretical.

Oxidation at room temperature with 32 g. of permanganate (4 atoms of oxygen) and with addition of 12 g. of potassium hydroxide gave 4·6 g. of anisic acid and 2·3 g. of anisaldehyde (semicarbazone, m. p. 216—217° corr.; Walbaum, *J. pr. Chem.*, 1903, **68**, 235, gives m. p. 203—204°).

Oxidation at 0° gave 6·6 g. of a mixture of anisic acid and anisylketocarboxylic acid and 0·85 g. of anisaldehyde.

Oxidation of pure anethole by Ladenburg and Fitz's method as applied to oil of anise, using potassium dichromate and sulphuric acid, gave a 47% yield of anisic acid.

3-*Nitro*-4-*anisoyl Chloride*.—3-Nitroanisic acid was prepared by Auwers's method (*Ber.*, 1897, **30**, 1477) by heating 20 g. of anisic acid with 200 c.c. of nitric acid (*d* 1·4) on the water-bath for 30 minutes. From 75 g. of anisic acid there were obtained 3·7 g. of a non-acidic fraction which on distillation gave 2·65 g., m. p. 54—55°, b. p. (external bath temperature) 170°/20 mm. These constants agree with those of 4-nitroanisole. The non-volatile residue (1·0 g.), on two crystallisations from alcohol, gave 2 : 4-dinitroanisole (0·45 g.), m. p. 87°. In another experiment which was strictly comparable with the nitration of *p*-toluic acid, there were isolated from the nitration of 20 g. of anisic acid, 20·2 g. of nitroanisic acid, m. p. 190°; by ether extraction of this nitro-acid in alkaline solution, 2·3 g. of nitroanisoles, m. p. 84°; and by ether extraction of the original aqueous mother-liquor, 1·45 g. of nitroanisoles, m. p. 45°. The nitroanisic acid was converted into 3-*nitro*-4-*anisoyl chloride* by phosphorus pentachloride. This boils at 210°/15 mm., is sparingly soluble in low-boiling petroleum, but readily soluble in warm ether, from which it crystallises in broad needles, m. p. 52·5—53·5° (corr.).

3′-*Nitro*-4′-*anisoyl*-4-*aminophenylarsinic Acid* (I; R = OMe).—This nitro-acid was prepared in the same way as the corresponding toluoyl derivative. The yield was 48·3%. It is soluble in boiling formic acid and crystallises therefrom in needles, but is sparingly soluble in boiling acetic acid, from which it separates in woolly needles (Found: As, 18·9. $C_{14}H_{13}O_7N_2As$ requires As, 18·9%).

3′-Amino-4′-anisoyl-4-aminophenylarsinic acid (II; R = OMe) was prepared exactly as described for the corresponding toluoyl derivative. The yield was 95%. When liberated from concentrated solutions of its salts with acids by means of saturated sodium acetate, it separates in a gelatinous state, but from dilute solutions in needles. The gelatinous form passes into the crystalline on contact with the needles. It is not soluble in acids weaker than 3*N* in the cold, but dissolves readily on warming. The most characteristic salt is the *hydrochloride*, which crystallises well in wedge-shaped plates. The *sulphate* separates in sphæro-crystals, the *nitrate* in microscopic, woolly needles. It diazotises and couples with alkaline β-naphthol with production of a bright red colour (Found: As, 20·2. $C_{14}H_{15}O_5N_2As$ requires As, 20·5%).

3′-Acetylamino-4′-anisoyl-4-aminophenylarsinic acid is most conveniently prepared by shaking the amino-acid, dissolved in *N*-sodium hydroxide (4 mols.), with excess of acetic anhydride. The yield is quantitative (Found: As, 18·8. $C_{16}H_{17}O_6N_2As$ requires As, 18·4%). This acid is almost insoluble in boiling acetic acid, but extremely soluble in cold 90% formic acid. From more dilute formic acid it separates, anisotropic, in sphæro-crystals. The maximum dose tolerated by mice is 1·5 mg. per g. of mouse. Attempts to prepare the propionyl derivative by the same method were fruitless.

Action of Sodium Formaldehydesulphoxylate on 3′-Amino-4′-anisoyl-4-aminophenylarsinic Acid.—The amino-acid (5·5 g.) was dissolved in 15 c.c. of *N*-sodium hydroxide (1 mol.) and 2·4 g. of pure sodium formaldehydesulphoxylate were added. The solution was heated for 15 minutes in boiling water, cooled, and poured into a large volume of spirit. A gum separated which was obtained in a solid powdery condition by grinding under absolute alcohol (yield 2·6 g.) (Found: Loss at 95°, 0·5; As, 15·8; S, 7·0. $C_{15}H_{15}O_7N_2SAsNa_2$ requires As, 15·4; S, 6·6%). This sodium salt, so prepared, has no free amino-groups. It is, however, unstable towards *N*-hydrochloric acid at 50° and evolves sulphur dioxide.

3′-Carbethoxyamino-4′-anisoyl-4-aminophenylarsinic acid was prepared by adding ethyl chloroformate (1·1 c.c.) in two portions to the amino-acid (3·7 g.) dissolved in 15 c.c. of *N*-sodium hydroxide. The product was acidified and the precipitated solid extracted with *N*-hydrochloric acid at 50° to remove diazotisable material (yield 3·7 g.) (Found: As, 17·5. $C_{17}H_{19}O_7N_2As$ requires As, 17·1%). The acid is practically insoluble in boiling acetic acid, but readily so in boiling 90% formic acid and crystallises therefrom in microscopic leaflets. The maximum dose tolerated by mice is 0·75 mg per g. of mouse.

The s-*Carbamide of* 3′-*Amino*-4′-*anisoyl*-4-*aminophenylarsinic Acid*.—The amino-acid (3·7 g.) dissolved in 100 c.c. of half-saturated sodium acetate solution with the aid of 5 c.c. of 2*N*-sodium hydroxide was shaken with several molecules excess of carbonyl chloride in toluene (35 c.c. of 12·5% solution). The product obtained on acidification was extracted with warm *N*-hydrochloric acid and precipitated finally from dilute ammonia by acid (yield 33%). This *carbamide* is precipitated in the gelatinous state from its salts. It is insoluble in boiling glacial acetic acid, but from boiling 90% formic acid, in which it is very sparingly soluble, it crystallises in microscopic needles (Found : As, 19·6. $C_{29}H_{28}O_{11}N_4As_2$ requires As, 19·8%).

3″-*Nitro*-4″-*anisoyl*-3′-*amino*-4′-*anisoyl*-4-*aminophenylarsinic Acid* (corresponding with IX; R = OMe).—Aminoanisoylaminophenylarsinic acid (7·3 g.) dissolved in 50 c.c. of 10% sodium hydroxide at − 5° was treated with 8·3 g. of nitroanisoyl chloride in 15 c.c. of toluene and stirred vigorously for 4½ hours. Toluene was removed and the aqueous solution acidified. The precipitated solid was extracted with *N*-hydrochloric acid to remove aminoarsinic acid. The dried solid was extracted with ether to remove nitroanisic acid and reprecipitated from dilute ammonia.

This complex nitro-arsinic acid is precipitated as a voluminous gelatinous solid from solutions of its salts. It is very sparingly soluble in boiling glacial acetic acid, but separates well in clusters of needles. It is somewhat more readily soluble in boiling 90% formic acid (Found : As, 13·6. $C_{22}H_{20}O_9N_3As$ requires As, 13·7%). The maximum dose tolerated by mice is 0·075 mg. per g. of mouse.

3″-*Amino*-4″-*anisoyl*-3′-*amino*-4′-*anisoyl*-4-*aminophenylarsinic Acid* (IX; R = OMe).—The nitro-acid (5·2 g.) was reduced in the usual way with ferrous chloride and alkali. The combined alkaline extracts of the ferric hydroxide were made neutral to Congo-paper. The precipitated solid was collected and whilst still damp made into a thin cream with water and added to 2000 c.c. of *N*-nitric acid (free from nitrous acid) at 50°. The solution was rapidly filtered, treated with charcoal, and refiltered. On addition of saturated sodium acetate solution the *amino-acid* was precipitated in an amorphous condition in 75% yield. This acid is soluble in hot *N*-hydrochloric acid and deposits an indefinitely crystalline but anisotropic solid on cooling. It is almost insoluble in boiling *N*-sulphuric acid, the *sulphate* crystallising in microscopic needles. In *N*-nitric acid it is soluble on heating and the *nitrate* crystallises in balls of needles (Found : As, 14·3. $C_{22}H_{22}O_7N_3As$ requires As, 14·5%). The maximum dose tolerated by mice is 0·02 mg. per g. of mouse.

3''-Nitrobenzoyl-3'-amino-4'-anisoyl-4-aminophenylarsinic acid (corresponding with IX; R = H) was prepared in the same way as the corresponding 3''-nitroanisoyl compound (above). From 7·3 g. of 3'-amino-4'-anisoylaminophenylarsinic acid and 3-nitrobenzoyl chloride (2 mols.) there were obtained 5·8 g. of the required acid as a gelatinous precipitate. It is sparingly soluble in boiling acetic or 90% formic acid, separating from the former in short, pointed needles and from the latter in square tablets (Found: As, 14·7. $C_{21}H_{18}O_8N_3As$ requires As, 14·6%). The maximum dose tolerated by mice is 0·1 mg. per g. of mouse.

3''-Aminobenzoyl-3'-amino-4'-anisoyl-4-aminophenylarsinic acid (IX; R = H) was prepared in the same way as the corresponding 3''-aminoanisoylarsinic acid, except that 1500 c.c. of *N*-nitric acid at 50° were sufficient to dissolve the amino-acid. The yield was 3·1 g. from 5·0 g. of nitro-acid. This complex amino-acid separates in needles when liberated from dilute acid solutions by addition of sodium acetate (Found: As, 15·4. $C_{21}H_{20}O_6N_3As$ requires As, 15·4%). With *N*-hydrochloric acid it forms a very sparingly soluble *hydrochloride* crystallising in microscopic rods. In 2*N*-sulphuric acid, it is readily soluble, the *sulphate* crystallising on keeping in fine, woolly needles; and in warm *N*-nitric acid, it dissolves and gives an indefinitely crystalline but anisotropic *nitrate* on cooling. The maximum dose tolerated by mice is 1·0 mg. per g. of mouse.

Nitration of 3'-Nitro-4'-anisoyl-4-aminophenylarsinic Acid.—This mononitro-arsinic acid was further mononitrated as described for the previous dinitro-arsinic acids. The product consisted of a mixture of 3' : 5'-dinitro-4'-anisoyl-4-aminophenylarsinic acid and 3 : 3'-dinitro-4'-anisoyl-4-aminophenylarsinic acid in the proportion of 3 : 7. These acids could not be separated by fractional crystallisation from 75% acetic acid nor by fractional crystallisation of the ammonium salts (Found: As, 17·0. $C_{14}H_{12}O_9N_3As$ requires As, 17·0%). The composition of the mixture was readily determined by hydrolysis as follows. Three g. of the dinitro-acids were boiled for an hour with 45 c.c. of *N*-sodium hydroxide and then neutralised to Congo-paper. The mixture of ether-soluble arsenic-free acids was not examined in detail, but 3 : 5-dinitro-4-hydroxybenzoic acid was identified. The ether-insoluble acids consisted of a mixture of a 4-aminophenylarsinic and 3-nitro-4-aminophenylarsinic acid. These could be separated almost quantitatively by making use of the observation that 4-aminophenylarsinic acid is readily soluble in 0·5*N*-hydrochloric acid, whereas the nitro-acid is not appreciably soluble. From the final aqueous mother-liquors of the hydrolysis, precipitation as magnesium salt in ammoniacal solution gave a further crop of 4-amino-

phenylarsinic acid. In this way, 1·25 g. of 3-nitro-4-aminophenylarsinic and 0·4 g. of 4-aminophenylarsinic acids were obtained, or 96% of the theoretical yield.

The reduction of the mixed dinitro-acids by ferrous chloride was unsatisfactory.

Hydrolysis of 4-Ethoxybenzonitrile.—(a) *By 75% sulphuric acid.* Twelve g. of the nitrile were boiled for 1 hour with 72 g. of sulphuric acid and 24 g. of water. Ether extraction of the mixture diluted with water gave 0·36 g. of a phenolic fraction, partly crystalline and giving a blue colour with ferric chloride in alcoholic solution and a violet colour in aqueous solution. The sulphuric acid liquors were worked up as barium salts, when, after removal of barium sulphate, a very soluble barium salt was isolated (yield 9 g.). On crystallisation from water, it separated in long, glistening needles of barium phenol-4-sulphonate. It was compared with a sample prepared by the action of sulphuric acid on phenol (Found on air-dried salt: loss at 95°, 9·3; on salt dried at 95°: Ba, 27·8. $C_{12}H_{10}O_8S_2Ba,3H_2O$ requires loss of $2\frac{1}{2}H_2O$, 8·4%. $C_{12}H_{10}O_8S_2Ba,\frac{1}{2}H_2O$ requires Ba, 27·9%).

If the original solution be treated with ether instead of water the free phenol-4-sulphonic acid crystallises, but is very hygroscopic (compare Allain, *Bull. Soc. chim.*, 1887, **47**, 879).

(b) *By 60% sulphuric acid.* Twelve g. of 4-ethoxybenzonitrile were boiled for 30 minutes with 56·5 g. of sulphuric acid and 37·5 c.c. of water. The solid obtained on pouring into water was separated by means of sodium carbonate solution into 3·1 g. of 4-ethoxybenzamide and 6·1 g. of 4-ethoxybenzoic acid. The amide was completely hydrolysed to the acid by boiling with 60% sulphuric acid for 2 hours.

3-Nitro-4-ethoxybenzoic Acid.—4-Ethoxybenzoic acid (21 g.) was heated with 210 c.c. of nitric acid (*d* 1·42) on the water-bath until solution had just been effected. The product was poured into water, the solid collected, dissolved for the most part in ammonia, and extracted with ether, which removed a low-melting, crystalline solid, A, weighing 3 g. The ammoniacal solution on acidification gave an 80% yield of *3-nitro-4-ethoxybenzoic acid.* This acid crystallises well from spirit in rectangular plates or rods, m. p. 200—201° (Found: C, 51·0; H, 4·4. $C_9H_9O_5N$ requires C, 51·2; H, 4·3%).

The ether-soluble material, A (4·5 g. from two batches), on fractional distillation under reduced pressure, gave 1·6 g., m. p. 58—59°, b. p. 188° (external bath temperature)/22 mm. The residue, 2·65 g., on recrystallisation from alcohol gave pure 2 : 4-dinitrophenetole, m. p. 83°, in excellent yield, whilst the low-

melting solid on crystallisation from alcohol melted at 62° and proved to be 4-nitrophenetole.

3-*Nitro*-4-*ethoxybenzoyl chloride* is very sparingly soluble in boiling petrol, but is more soluble in dry ether, from which it crystallises in slender prisms, m. p. 81—82° (corr.). It boils at 215—216° (corr.)/20 mm.

3′-*Nitro*-4′-*ethoxybenzoyl*-4-*aminophenylarsinic acid* (I; R = OEt) was prepared in the same way as the corresponding 4′-chloro-derivative, using method 5. The yield was 49%. It is very sparingly soluble in boiling acetic acid and sparingly in 90% formic acid. It crystallises in fine needles (Found: As, 18·5. $C_{15}H_{15}O_7N_2As$ requires As, 18·3%).

3′-*Amino*-4′-*ethoxybenzoyl*-4-*aminophenylarsinic Acid* (II; R = OEt).—The mononitro-acid (8·2 g.) was reduced as described for the corresponding 4′-toluoyl compound. On neutralisation of the alkaline extracts of the ferric hydroxide to Congo-paper, the acid was precipitated in an amorphous condition. When dissolved in 200 c.c. of *N*-hydrochloric acid at 45° and precipitated by addition of saturated sodium acetate, it separated crystalline (yield 5·8 g.). The original mother-liquors gave a further crop of 0·7 g. of acid by precipitation as the magnesium salt from hot ammoniacal solution (total yield 86%). This *amino-acid* crystallises in microscopic, woolly needles (Found: As, 19·3. $C_{15}H_{17}O_5N_2As$ requires As, 19·7%). It is soluble in warm *N*-hydrochloric acid, but very sparingly soluble in hot 3*N*-acid through formation of the *hydrochloride*, which crystallises as a sandy powder composed of small tablets. It is soluble in 2*N*-sulphuric acid, but rapidly crystallises as the *sulphate* in small, pointed prisms. In 3*N*-nitric acid it is readily soluble and the *nitrate* crystallises from concentrated solution in fine needles. The diazotised acid couples with alkaline β-naphthol with production of a bright red colour.

Nitration of 3′-*Nitro*-4′-*ethoxybenzoyl*-4-*aminophenylarsinic Acid*.—This acid was re-nitrated as described for the corresponding 4′-anisoylarsinic acid. A mixture of 3 : 3′-dinitro-4′-ethoxybenzoyl-4-aminophenylarsinic and 3′ : 5′-dinitro-4′-ethoxybenzoyl-4-aminophenylarsinic acids in the ratio 5 : 3 was obtained, as was proved by hydrolysis and quantitative separation of the arsinic acids as described for the anisoyl acids (Found: As, 16·5. $C_{15}H_{14}O_9N_3As$ requires As, 16·5%).

4′-*Chloro*-3′-*nitrobenzoyl*-4-*aminophenylarsinic Acid* (I; R = Cl).—4-Chloro-3-nitrobenzoic acid was prepared in 90% yield by heating 4-chlorobenzoic acid with nitric acid (*d* 1·5; 4 vols.) on the water-bath until solution was effected; 20 g. of chlorobenzoic acid gave 23·6 g. of chloronitrobenzoic acid, m. p. 180°, and as a

by-product 0·22 g. of *p*-chloronitrobenzene, m. p. 77°, by extraction of the acid in alkaline solution, and 0·5 g. of *p*-chloronitrobenzene, m. p. 82°, by extraction of the original aqueous mother-liquors made alkaline. Boiling nitric acid (*d* 1·42) has no action on 4-chlorobenzoic acid. The acid chloride was prepared in the usual way, b. p. (external bath temperature) 180—190°/20—22 mm. It was introduced with difficulty into 4-aminophenylarsinic acid by the Schotten-Baumann method, using two molecular proportions of acid chloride. A variety of conditions to improve the yield were tried.

No.	Solvent.	Temperature.	Sodium Hydroxide.	Yield %.
1	Benzene	20—25°	10%	32
2	None	20—50	,,	18
3	Benzene	0—10	,,	40
4	Benzene	20—30	5%	22
5	Toluene	−5—0	,,	40

Unchanged nitrochlorobenzoic acid was readily recovered by ether extraction, and unused 4-aminophenylarsinic acid by neutralising the aqueous mother-liquors to Congo-paper and evaporating until sodium chloride began to separate.

4′-Chloro-3′-nitrobenzoyl-4-aminophenylarsinic acid is very sparingly soluble in boiling acetic acid, more readily in boiling 90% formic acid, from which it crystallises well, in needles (Found: Cl, 8·6. $C_{13}H_{10}O_6N_2ClAs$ requires Cl, 8·8%).

4′-Chloro-3′-aminobenzoyl-4-aminophenylarsinic Acid (II; R = Cl).—The nitro-acid (6·65 g.) was reduced with ferrous chloride (7 mols.) at − 5° as described for the toluoyl compound. The combined filtrates from the ferric hydroxide extractions, on being made neutral to Congo-paper, deposited the amino-acid in a crystalline condition mixed with a small quantity of amorphous impurity. The amount contained in the mother-liquors and precipitable as magnesium salt was negligible. The crude acid was heated at 80° with 800 c.c. of 3*N*-hydrochloric acid; the amino-acid then dissolved. On addition of saturated sodium acetate to the rapidly filtered solution, the *amino-acid* separated in leaflets (yield 80%) (Found: Cl, 9·4. $C_{13}H_{12}O_4N_2ClAs$ requires Cl, 9·6%). It is very sparingly soluble in 3*N*-hydrochloric acid at 100°, but from stronger acid the *hydrochloride* crystallises in oval leaflets. In boiling 2*N*-sulphuric acid it is insoluble, but from a much stronger acid the *sulphate* crystallises in square tablets. It is soluble in hot 3*N*-nitric acid, and this solvent, freed from nitrous acid, would probably be preferable to hydrochloric acid for its extraction in the above preparation. The diazotised acid couples with alkaline β-naphthol with production of a bright red colour.

4′-Chloro-3 : 3′-dinitrobenzoyl-4-aminophenylarsinic Acid (III; R = Cl).—The mononitro-acid (8 g.) dissolved in 24 c.c. of sulphuric

acid was nitrated at − 5° with 2 g. of sulphuric acid and 2 g. of nitric acid (*d* 1·42); the mixture, when at room temperature, was poured on to ice. The product was collected, dried, and digested on the boiling-water bath with 40 c.c. of glacial acetic acid for ½ hour; it then became crystalline (yield 8·5 g.) (Found: Cl, 8·1. $C_{13}H_9O_8N_3ClAs$ requires Cl, 8·0%). The acid is very sparingly soluble in boiling glacial acetic acid, somewhat more soluble in boiling 90% formic acid, from which it crystallises well in needles.

Hydrolysis of 4′-*Chloro*-3 : 3′-*dinitrobenzoyl*-4-*aminophenylarsinic Acid*.—Two g. of the dinitro-acid were boiled for 30 minutes with 30 c.c. of *N*-sodium hydroxide. When cold, the solution was neutralised to Congo-paper and the precipitated acids were collected, dried, and extracted with dry ether in a Soxhlet apparatus. The ether-soluble acid weighed 1·0 g., m. p. 175°. A mixture of the substance with 4-chloro-3-nitrobenzoic acid, which itself melted at 182°, melted at 177°. The ether-insoluble material weighed 1·1 g. and was unchanged in weight after extraction with 0·5*N*-hydrochloric acid to remove any possible 4-aminophenylarsinic acid. This proved to be 3-nitro-4-aminophenylarsinic acid. The original aqueous solution on ether extraction gave 0·05 g. of crystalline acid, m. p. 172°. Mixed with chloronitrobenzoic acid, this melted at 157°; with 3-nitro-4-hydroxybenzoic acid, m. p. 185°, however, the melting point was raised to 175°.

4′-*Chloro*-3 : 3′-*diaminobenzoyl*-4-*aminophenylarsinic Acid* (IV; R = Cl).—The dinitro-acid (6·5 g.) was reduced exactly as described for the corresponding dinitrotoluoylarsinic acid. The combined alkaline extracts of the ferric hydroxide, when neutralised to Congo-paper, gave an amorphous, brown precipitate, but on keeping a few hours the diamino-acid (3·0 g.) crystallised. The filtrate was made alkaline with ammonia and heated with magnesium chloride; a magnesium salt then separated which gave an additional 1·25 g. of acid. The combined crude acids were dissolved in 40 c.c. of *N*-hydrochloric acid with addition of 1 c.c. of concentrated acid and precipitated by addition of saturated sodium acetate until neutrality to Congo-paper was reached (yield 76%). The acid so prepared crystallises in rosettes of pointed plates (Found: Cl, 9·2. $C_{13}H_{13}O_4N_3ClAs$ requires Cl, 9·2%).

Preparation and Nitration of 4-*Ethylcarbonatobenzoic Acid*.—4-Hydroxybenzoic acid (34·5 g.) dissolved in 500 c.c. of *N*-sodium hydroxide (2 mols.) was shaken with 26·0 c.c. of ethyl chloroformate (1·1 mols.), added in four portions. Ether extraction removed a viscous, pleasant-smelling oil (2·6 g.), presumably

$$EtO_2C{\cdot}O{\cdot}C_6H_4{\cdot}CO_2{\cdot}CO_2Et$$

(compare analogous case of salicylic acid, D.R.-P. 117,267). The

aqueous solution on acidification gave 49·3 g. of 4-*ethylcarbonatobenzoic acid* (94% yield). This acid is best recrystallised from 85 volumes of boiling water and separates in long, glistening needles, m. p. 154—156°. It is very soluble in the usual organic solvents (Found: C, 57·0; H, 4·9. $C_{10}H_{10}O_5$ requires C, 57·1; H, 4·8%). *Nitration.* The acid (48·5 g.) was dissolved in 182 c.c. of fuming nitric acid (nitric acid, *d* 1·42, has no action) and heated for 10 minutes on the boiling-water bath. The product was poured into water, the solid collected, dissolved in sodium bicarbonate solution, and extracted with ether, which removed 7·5 g. of non-acidic solid, A. The aqueous solution on acidification gave 44·6 g. (76% yield) of 3-*nitro*-4-*ethylcarbonatobenzoic acid*. This is best recrystallised from 15 volumes of boiling benzene and separates in clear, irregular-shaped plates, m. p. 168—169° (Found: C, 47·3; H, 3·7. $C_{10}H_9O_7N$ requires C, 47·1; H, 3·6%).

The non-acidic solid, A, was distilled in a vacuum, when 6·35 g. passed over at 18 mm. and an external bath temperature of 192°. This fraction, on crystallisation from alcohol, separated readily in fine needles, m. p. 67—68° (corr.) in agreement with the properties described by Ransom (*Ber.*, 1898, **31**, 1064) for ethyl 4-nitrophenylcarbonate. On hydrolysis with alcoholic soda, it yielded 4-nitrophenol. The non-volatile residue, 1·6 g., was highly coloured and did not crystallise on keeping, but was proved to be *ethyl* 2 : 4-*dinitrophenylcarbonate* by hydrolysis with alcoholic sodium hydroxide, which gave 2 : 4-dinitrophenol.

3′-*Nitro*-4′-*ethylcarbonatobenzoyl*-4-*aminophenylarsinic Acid* (V).—The above-described 3-nitro-4-ethylcarbonatobenzoic acid (25·5 g.) was shaken with 21·0 g. of phosphorus pentachloride until reaction took place. The phosphorus oxychloride was removed under reduced pressure by gentle warming. The residual syrupy *nitroethylcarbonatobenzoyl chloride*, which crystallises readily in a freezing mixture and remains solid above room temperature, after being evaporated to dryness once or twice with dry ether, was added in three portions with vigorous shaking to 15·5 g. of sodium 4-aminophenylarsinate pentahydrate dissolved in 300 c.c. of half-saturated sodium acetate solution. The solid (34 g.) precipitated by making the solution definitely acid to Congo-paper, was divided by ether extraction into 15·6 g. of unchanged nitro-acid and 18·1 g. (80% yield) of the required *arsinic acid*. This acid is soluble in boiling acetic acid, more readily soluble in boiling 90% formic acid, and crystallises in needles (Found: As, 16·5. $C_{16}H_{15}O_9N_2As$ requires As, 16·5%).

3′-*Nitro*-4′-*hydroxybenzoyl*-4-*aminophenylarsinic Acid* (VI).—The crude acid (18·1 g.) as obtained above was dissolved in 160 c.c. of

N-sodium hydroxide, and the solution just brought to its boiling point. Addition of acid to the cold solution precipitated, at an intermediate stage, the *sodium* salt of the nitrohydroxy-acid in rectangular plates, but finally (acid to Congo-paper) the free acid as a primrose-yellow solid (yield 97%). This acid is sparingly soluble in boiling acetic acid, crystallising therefrom in minute clusters of needles, but readily soluble in boiling 90% formic acid, from which it crystallises in long, silky needles (Found : As, 19·4. $C_{13}H_{11}O_7N_2As$ requires As, 19·6%).

Reduction of 3′-Nitro-4′-hydroxybenzoyl-4-aminophenylarsinic Acid.—(a) *By hyposulphite.* The nitro-acid (3·8 g.) in 25 c.c. of *N*-sodium hydroxide (2·5 mols.) was treated with 6 g. of sodium hyposulphite added in portions. The end-point was determined by removing samples and observing the absence of yellow colour on adding alkali. The separated solid, consisting mainly of the sodium salt of the required amino-acid, was collected and dissolved in 240 c.c. of *N*-hydrochloric acid at 50°. The filtrate, made neutral to Congo-paper by addition of saturated sodium acetate solution, deposited the pure amino-acid (2·1 g.) in small needles.

(b) *By ferrous chloride.* This reagent, used as frequently described in this paper, reduced the nitro-acid very smoothly. The amino-acid was obtained quite pure in 93·5% yield by neutralisation of the alkaline filtrate from the ferric hydroxide.

3′-Amino-4′-hydroxybenzoyl-4-aminophenylarsinic acid is readily soluble in warm *N*-hydrochloric, nitric, or sulphuric acid, the salts of the former two crystallising in needles, that of the latter being amorphous and gelatinous. The acid diazotises with production of a pale yellow colour and even from very dilute solutions the *diazo-oxide* separates in pale yellow needles. This couples with alkaline β-naphthol with a cherry-red colour. The acid is soluble in saturated sodium hydrogen carbonate solution, but the *sodium* salt soon separates in micro-crystals (Found : As, 21·5. $C_{13}H_{13}O_5N_2As$ requires As, 21·3%).

3′-Amino-4′-hydroxybenzoyl-4-aminoarsenobenzene (VIII).—Amino-hydroxybenzoylaminophenylarsinic acid (3·3 g.) was suspended in 16·5 c.c. of hypophosphorous acid (*d* 1·137) with addition of 33 c.c of 50% acetic acid and a crystal of potassium iodide. The mixture was stirred at 50—55° for 1 hour; the whole of the originally crystalline suspension had then become orange-yellow and amorphous. The product was centrifuged off, washed several times with air-free water, and treated with sodium hydrogen carbonate solution until permanently alkaline. The liberated base was re-centrifuged, well washed, and dried in a vacuum (yield 2·7 g.). This arseno-derivative is soluble instantly in sodium hydroxide,

but not in sodium carbonate. It is insoluble in hydrochloric acid of any strength, but vanishes almost instantly on addition of nitrite with intermediate development of a deep colour. It then couples with alkaline β-naphthol (Found: As, 24·7, 25·1. $C_{26}H_{22}O_4N_4As_2$ requires As, 24·8%).

3′-Acetylamino-4′-acetoxylbenzoyl-4-aminophenylarsinic Acid.—The aminohydroxy-acid (3·5 g.) was dissolved in 40 c.c. of *N*-sodium hydroxide or sodium carbonate, and 5 c.c. of acetic anhydride were added in 1 c.c. portions with vigorous shaking. The solution was acidified to Congo-paper, and the precipitated solid well washed with water and dried (yield 3·8 g.). From weakly alkaline solution this acid is precipitated in fine needles which are almost insoluble in boiling glacial acetic acid but extremely soluble in cold 90% formic acid. From more dilute formic acid it crystallises well in fine, soft needles (Found: As, 16·9. $C_{17}H_{17}O_7N_2As$ requires As, 17·2%). The maximum dose tolerated by mice is 1·75 mg. per g. of mouse.

3′-Acetylamino-4′-hydroxybenzoyl-4-aminophenylarsinic Acid.—When a solution of 1 g. of the preceding acid in 10 c.c. of *N*-sodium hydroxide (4 mols.) was kept for 20 hours at room temperature, then diluted, and acidified with 3*N*-hydrochloric acid, the N-*acetyl acid* was obtained as a microcrystalline, anisotropic powder (Found: As, 19·2. $C_{15}H_{15}O_6N_2As$ requires As, 19·0%). This acid is almost insoluble in boiling glacial acetic acid, but very readily soluble in warm 90% formic acid, from which it separates in microscopic needles.

3-Acetylamino-4-acetoxyphenylarsinic Acid.—3-Amino-4-hydroxyarsinic acid (2·33 g.; 0·01 mol.) was dissolved in 25 c.c. of water with the aid of 3·5 g. (4 mols.) of sodium bicarbonate and acetylated by addition in 1 c.c. portions of 5 c.c. of acetic anhydride. When the solution was acidified with strong hydrochloric acid, the arsinic acid separated in needles (yield 2·5 g.). It is soluble in boiling glacial acetic acid and readily soluble in cold 90% formic acid (Found: As, 23·7. $C_{10}H_{12}O_6NAs$ requires As, 23·6%).

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CCCLXII.—*The Action of Nitrous Acid upon Amides and Other "Amino"-compounds.*

By ROBERT HENRY ADERS PLIMMER.

THE action of nitrous acid upon amino-compounds was apparently first used by Sachsse and Kormann (*Landw. Versuchs-Stat.*, 1874, **17**, 321) for the detection and estimation of these compounds in plant extracts. H. T. Brown (*Trans. Guinness Res. Lab.*, 1903)

employed the reaction for studying the formation of amino-acids in the brewing process, and improved the old type of apparatus. Not until Van Slyke (*J. Biol. Chem.*, 1911, **9**, 185; 1912, **12**, 275) devised a satisfactory apparatus for the estimation was the method extensively used, and, as is well known, its chief use is for distinguishing the different forms of nitrogen contained in the amino-acids resulting from the hydrolysis of proteins. A special short analysis of proteins can be made by the method of Van Slyke (*J. Biol. Chem.*, 1911, **10**, 15).

The earlier workers tested only a few amino-acids; leucine and alanine gave off the whole of their nitrogen as nitrogen gas, asparagine gave off only half of its nitrogen as gas. Van Slyke tested a considerable number of amino-compounds. All α-amino-acids reacted rapidly; presumably, therefore, the α-amino-group, but not the amide group, of asparagine reacted. The nitrogenous groups of guanidine and creatine did not react, nor the guanidine group of arginine. The ε-amino-group of lysine reacted slowly, as also the amino-groups of certain purines. Dunn and Schmidt (*J. Biol. Chem.*, 1922, **53**, 401) and Wright Wilson (*J. Biol. Chem.*, 1923, **56**, 183) have further studied these slow reactions. Urea was found by Van Slyke to react slowly with sodium nitrite and acetic acid. Werner (J., 1917, **111**, 863), working under different conditions, found no reaction in the presence of acetic acid, but obtained an evolution of nitrogen in the presence of mineral acid. He found that the reaction was never complete and considered that the method was of no value for estimating urea. Krall (J., 1915, **107**, 1396) observed an evolution of nitrogen from guanidine in the presence of mineral acid, and Wright Wilson (*loc. cit.*) obtained nitrogen from creatinine, using the Van Slyke apparatus. No other reference to the reaction of nitrous acid with "amino"-compounds has been found on looking through the literature, except the statement in the text-book of Organic Chemistry by Meyer and Jacobson (1907, I, part 1) that amides give off nitrogen in the presence of strong sulphuric acid.

These experiments were therefore undertaken to find out the conditions under which amides, guanidine, and other amino-compounds react with nitrous acid and to reconcile the various discrepancies in the previous results. Some other amino-compounds besides the above-mentioned were also tested.

Experimental.

The large form of apparatus described by Van Slyke was used in all the experiments. After the removal of air from the apparatus the acetic acid–sodium nitrite mixture was always brought to the

same level in the reaction chamber; its volume measured 12 c.c. Generally 5 c.c., sometimes 10 c.c., of the solution of the compound under investigation were delivered from a pipette into the burette of the apparatus and run into the reaction chamber; the burette was then washed twice with 1 c.c. of water, and the washings were run into the apparatus. Reaction was allowed to proceed for periods varying from 1 to 24 hours; during the short periods the apparatus was continuously shaken, during the long periods it was shaken for the last half-hour. If the volume of gas evolved tended to fill the gas burette, the gas was passed into the permanganate vessel for absorption of nitric oxide and not returned to the burette until the reaction time was completed. In the experiments with mineral acid concentrated hydrochloric acid was added, 1 c.c. at a time, in the same way as the water used in washing the burette and in its stead. After the addition of 3 c.c. of hydrochloric acid gas evolution was very rapid, still more rapid after 4 c.c. In these cases the evolved gas was quickly passed into the permanganate vessel and further quantities were added only when the rate of gas evolution diminished. The rapid gas evolution usually ceased after 5 to 10 minutes, and became slow after 1 to 2 hours, so that the apparatus could be safely left for the long reaction periods amounting to 24 hours. The evolved nitrogen gas was finally measured and by the use of Van Slyke's table its amount was converted into mg. of nitrogen. Usually 1% solutions of the compound under examination were used. The total amount of nitrogen in these solutions was determined by a Kjeldahl estimation in another aliquot portion. All the figures of the estimations were calculated to g. of nitrogen per 100 c.c. of solution. The results of the experiments are in the following tables.

Discussion of Results.

Amides.—The experiments with the above amides show clearly that these do not give off an appreciable quantity of nitrogen with nitrous acid in the presence of acetic acid in 24 hours, and are thus sharply distinguished from the simple amino-acids, which were shown by Van Slyke to react rapidly and completely in from 5 to 30 minutes. The difference in behaviour is clearly shown with asparagine; only one amino-group reacts in a period of 23 hours under these conditions.

On introducing hydrochloric acid to the reaction mixture, complete reaction of the amide group did not occur until 5 c.c. of concentrated acid had been added. This amount of acid gave a concentration of approximately 2*N*-HCl. In the case of asparagine, the whole of its nitrogen was then evolved as gas.

Amides.

Formamide.

Expt. 1. *Total N per* 100 *c.c.* = 0·2884 *g.*

With	Time (hours).	Temp.	N evolved (g. per 100 c.c.).	% of total N.
2 c.c. H_2O	1·5	15°	0·0088	3·1
,, ,,	2·5	16	0·0080	2·8
,, ,,	24·5	16	0·0092	3·2

Expt. 2. *Total N per* 100 *c.c.* = 0·1806 *g.*

2 c.c. HCl	19	11	0·0191	10·6
4 ,, ,,	24	15	0·0923	51·1
6 ,, ,,	6	18	0·1609	89·1
6 ,, ,,	19	14	0·1427	79·0
6 ,, ,,	22	15	0·1805	100·0

Expt. 3. *Total N per* 100 *c.c.* = 0·2240 *g.*

2 c.c. H_2O	25	17	0·0162	7·2
2 ,, HCl	24	16	0·0234	10·3
3 ,, ,,	24·5	16	0·0228	10·2
3 ,, ,,	24	15	0·0344	15·4
4 ,, ,,	22	14	0·0604	27·0
5 ,, ,,	22	13	0·1415	63·2
6 ,, ,,	23	13	0·1732	77·3
7 ,, ,,	26	12	0·1882	84·0
7 ,, ,,	24	13	0·2139	95·5

Propionamide.

Expt. 1. *Total N per* 50 *c.c.* = 0·1155 *g.*

2 c.c. H_2O	0·5	13	0·0006	0·5
2 ,, ,,	2	14	0·0017	1·5
2 ,, ,,	17·5	14	0·0039	3·4
2 ,, ,,	46·5	13	0·0037	3·2

Expt. 2. *Total N per* 100 *c.c.* = 0·1946 *g.*

2 c.c. H_2O	23	11	0·0014	0·7
2 ,, HCl	25	11	0·0156	8·0
3 ,, ,,	23	11	0·0154	8·0
4 ,, ,,	23	12	0·1491	76·6
5 ,, ,,	22	12	0·1967	101·0

Acetamide.

Expt. 1. *Total N per* 100 *c.c.* = 0·1512 *g.*

With	Time (hours).	Temp.	N evolved (g. per 100. c.c.).	% of total N.
2 c.c. H_2O	1	12°	0·0011	0·7
2 ,, ,,	4·5	13	0·0011	0·7
2 ,, ,,	17·5	11	0·0011	0·7

Expt. 2. *Total N per* 100 *c.c.* = 0·1148 *g.*

2 c.c. H_2O	23	17	0·0032	2·8
2 ,, HCl	24	17	0·0082	7·1
3 ,, ,,	24	17	0·0360	31·3
4 ,, ,,	5	17	0·0644	56·1
4 ,, ,,	8	16	0·0696	60·6
4 ,, ,,	12	17	0·0882	76·8
4 ,, ,,	25	17	0·1042	90·7
5 ,, ,,	6	17	0·0964	83·9
5 ,, ,,	17	17	0·1112	96·9
5 ,, ,,	24	18	0·1185	103·2

Asparagine.

Expt. 1. *Total N per* 100 *c.c.* = 0·2100 *g.*

2 c.c. H_2O	0·25	17	0·1039	49·5
2 ,, ,,	0·5	15	0·1043	49·7
2 ,, ,,	1·0	15	0·1060	50·5
2 ,, ,,	3·5	16	0·1093	53·0
2 ,, ,,	17·5	13	0·1112	53·0

Expt. 2. *Total N per* 100 *c.c.* = 0·2100 *g.*

1 c.c. HCl	1	18	0·1061	50·5
2 ,, ,,	2·0	18	0·1079	57·4
3 ,, ,,	18·0	15	0·1135	54·0
5 ,, ,,	7·0	14	0·1615	76·9
7 ,, ,,	23·0	16	0·2209	105·2
8 ,, ,,	23	15	0·2142	102·0

Expt. 3. *Total N per* 100 *c.c.* = 0·3115 *g.*

2 c.c. H_2O	23·5	13	0·1699	54·5
2 ,, HCl	23	13	0·1842	59·1
3 ,, ,,	23	13	0·1917	61·5
4 ,, ,,	23	12	0·1861	59·7
5 ,, ,,	23·5	13	0·3014	96·7
6 ,, ,,	23·5	15	0 3264	104·4

Urea and Derivatives.

Urea.

Expt. 1. *Total N per* 100 *c.c.* = 0·2856 *g.*

With	Time (hours.)	Temp.	N evolved (g. per 100 c.c.).	% of total N.
2 c.c. H_2O	0·5	11°	0·0164	5·7
2 ,, ,,	1·0	11	0·0329	11·5
2 ,, ,,	2·5	12	0·0958	33·5
2 ,, ,,	3·5	12	0·1552	54·3
2 ,, ,,	6·5	12	0·2198	77·0
2 ,, ,,	8·5	11	0·2315	81·1
2 ,, ,,	15·0	11	0·2657	93·0
2 ,, ,,	24·5	10	0·2767	96·9

Expt. 2. *Total N per* 100 *c.c.* = 0·2422 *g.*

2 c.c. H_2O	8·5	20	0·2512	103·7
2 ,, ,,	23·0	18	0·2495	103·0
2 ,, ,,	47·0	19	0·2456	101·4

Biuret.

Expt. 1. *Total N per* 100 *c.c.* = 0·2884 *g.*

2 c.c. H_2O	1·0	11	0·0117	4·1
2 ,, ,,	5·5	11	0·0326	11·3
2 ,, ,,	16·5	11	0·0476	16·5
2 ,, ,,	40	11	0·0542	18·8

Expt. 2. *Total N per* 100 *c.c.* = 0·1554 *g.*

2 c.c. H_2O	6	21	0·0566	36·4
2 ,, ,,	17	19	0·0708	49·3
2 ,, ,,	23	22	0·0763	45·6
2 ,, HCl	24·5	21	0·1035	66·6
3 ,, ,,	23	22	0·1116	71·8
4 ,, ,,	24	20	0·1439	92·6
5 ,, ,,	23	19	0·1411	90·8
6 ,, ,,	24	17	0·1448	93·3

Urethane.

Expt. 1. *Total N per* 100 *c.c.* = 0·1764 *g.*

With	Time (hours).	Temp.	N evolved (g. per 100 c.c.).	% of total N.
2 c.c. H_2O	1	15°	0·0023	1·3
2 ,, ,,	3·5	16	0·0061	3·5
2 ,, ,,	23·5	8	0·0165	9·4

Expt. 2. *Total N per* 100 *c.c.* = 0·1862 *g.*

2 c.c. H_2O	23	15	0·0568	30·5
1 ,, HCl / 1 ,, H_2O	23	14	0·0929	49·9
2 ,, HCl	24	12	0·1137	61·1
3 ,, ,,	23·5	14	0·1309	70·2
4 ,, ,,	23	14	0·2143	115·1

Semicarbazide hydrochloride.

Expt. 1. *Total N per* 100 *c.c.* = 0·0658 *g.*

2 c.c. H_2O	0·5	14	0·0081	12·3
2 ,, ,,	1·5	15	0·0080	12·2
2 ,, ,,	17·5	14	0·0132	20·1

Expt. 2. *Total N per* 100 *c.c.* = 0·1904 *g.*

2 c.c. H_2O	0·5	14	0·0161	8·4
2 ,, ,,	2·5	15	0·0304	16·0
2 ,, ,,	4·5	15	0·0320	16·8
2 ,, ,,	16·5	14	0·0515	27·0
2 ,, ,,	4·5	15	0·0714	37·5

Expt. 3. *Total N per* 100 *c.c.* = 0·1218 *g.*

2 c.c. H_2O	25	16	0·0689	58·6
2 ,, HCl	23	22	0·0764	62·7
2 ,, ,,	23·5	17	0·0613	50·3
3 ,, ,,	24	18	0·0595	48·8
3 ,, ,,	23	19	0·0453	37·2
4 ,, ,,	24	17	0·2037	167·2
5 ,, ,,	24	18	0·2817	231·3
6 ,, ,,	23	20	0·2859	234·7

Guanidine and Derivatives.

Guanidine carbonate.

Expt. 1. *Total N per* 100 *c.c.* = 0·1316 *g.*

With	Time (hours).	Temp.	N evolved (g. per 100 c.c.).	% of total N.
2 c.c. H_2O	1·0	15°	0·0029	2·2
2 „ „	3·5	15	0·0016	1·2
2 „ „	5·5	15	0·0029	2·2
2 „ „	15·5	11	0·0060	4·6
2 „ „	40·5	14	0·0104	7·9

Expt. 2. *Total N per* 100 *c.c.* = 0·3185 *g.*

2 c.c. H_2O	25	13	0·0319	10·0
2 „ HCl	24	11	0·0639	20·1
4 „ „	23	11	0·1008	31·6
5 „ „	24	12	0·2481	77·9
6 „ „	24	10	0·2553	80·1
7 „ „	24	13	0·2784	87·4

Expt. 3. *Total N per* 100 *c.c.* = 0·2968 *g.*

2 c.c. H_2O	24	10	0·0104	3·5
2 „ HCl	23·5	9	0·0368	12·4
3 „ „	23·5	10	0·0437	14·7
4 „ „	23·5	11	0·0826	27·8
5 „ „	25	11	0·2132	71·8
6 „ „	24	12	0·2420	81·5
7 „ „	23·5	14	0·2622	88·4
8 „ „	23	14	0·2688	90·5

Arginine Carbonate.

Expt. 1. *Total N per* 100 *c.c.* = 0·1078 *g.*

2 c.c. H_2O	0·5	16	0·0267	24·8
2 „ „	1	16	0·0294	27·3
2 „ „	1	15	0·0280	26·0
2 „ „	1	16	0·0267	24·8
2 „ „	2	14	0·0280	26·0
2 „ „	4	14	0·0304	28·2
2 „ „	21·5	17	0·0504	46·7
2 „ HCl	4	19	0·0402	37·3
2 „ „	26	16	0·0698	64·7
2 „ „	30	16	0·0680	63·1

Creatine.

Expt. 1. *Total N per* 100 *c.c.* = 0·07 *g.*

2 c.c. H_2O	1	15	0·0018	2·6
2 „ „	3·5	15	0·0011	1·6
2 „ „	4·0	15	0·0023	3·3
2 „ „	18·5	15	0·0045	6·4

Expt. 2. *Total N per* 100 *c.c.* = 0·1456 *g.*

2 c.c. H_2O	23·5	14	0·0231	15·9
2 „ HCl	25	14	0·0394	27·0
3 „ „	24	14	0·0494	33·9
4 „ „	24	16	0·0483	33·2
4 „ „	24	13	0·0574	39·4
5 „ „	24	14	0·0967	66·4
6 „ „	24	15	0·1081	74·2
7 „ „	24	14	0·1008	69·2

Ammonium acetate.

Total N per 100 *c.c.* = 0·3304 *g.*

2 c.c. H_2O	0·5	13	0·1061	32·1
2 „ „	2·5	16	0·3385	102·4
2 „ „	18·5	14	0·3408	103·1

Aminoguanidine Acetate.

Expt. 1. *Total N per* 100 *c.c.* = 0·2590 *g.*

With	Time (hours).	Temp.	N evolved (g. per 100 c.c.).	% of total N.
2 c.c. H_2O	0·5	12°	0·0177	6·8
2 „ „	1·5	11	0·0465	17·9
2 „ „	2·5	14	0·0510	19·7
2 „ „	17·5	11	0·0608	23·5
2 „ „	24·5	15	0·0617	23·8
2 „ „	25·5	15	0·0659	25·4
2 „ „	48·5	11	0·0709	27·4
2 „ „	50	15	0·0777	30·0

Expt. 2. *Total N per* 100 *c.c.* = 0·3402 *g.*

2 c.c. H_2O	24	13	0·0731	21·5
2 „ HCl	24	13	0·1052	30·9
3 „ „	24	12	0·1067	31·4
4 „ „	24	12	0·1855	54·5
5 „ „	24	12	0·2750	80·8
6 „ „	25	14	0·3112	91·5
7 „ „	24	16	0·3168	93·3
8 „ „	24	16	0·3154	92·7

Arginine carbonate.

Expt. 2. *Total N per* 100 *c.c.* = 0·1211 *g.*

2 c.c. H_2O	0·5	20	0·0212	17·5
2 „ „	1·0	19	0·0266	22·0
2 „ „	24	13	0·0566	46·7
2 „ HCl	24	14	0·1044	86·2
3 „ „	24·5	13	0·1006	83·1
4 „ „	24·5	14	0·1118	92·3
6 „ „	24	15	0·1173	96·9
7 „ „	25	19	0·1167	96·4
8 „ „	24	17	0·1237	102·1

Creatinine.

Expt. 1. *Total N per* 100 *c.c.* = 0·2898 *g.*

2 c.c. H_2O	1	15	0·0766	22·9
2 „ „	4	17	0·1027	35·4
2 „ „	15·5	15	0·1075	37·1
2 „ „	23	17	0·1164	40·1
2 „ „	25	19	0·1211	41·8
2 „ HCl	25	17	0·1208	41·7
3 „ „	24	13	0·1221	42·1
4 „ „	23	14	0·0886	30·6
5 „ „	24	16	0·0540	18·6
6 „ „	25	14	0·0646	22·3
6 „ „	23	17	0·0478	16·5
7 „ „	24	15	0·0506	17·5
8 „ „	23	14	0·0455	15·7

Hydrazine sulphate.

Total N per 100 *c.c.* = 0·0574 *g.*

2 c.c. H_2O	0·5	13	0·0641	111·7
2 „ „	4·5	13	0·1424	258·5
2 „ „	17·5	14	0·1573	274·0

The formation of nitrogen in the presence of hydrochloric acid is not due to hydrolysis of the amide. Experiments were made to test this possibility by allowing 20 c.c. of the amide solution to stand for 24 hours with 6 c.c. of concentrated hydrochloric acid. The solution was then rendered alkaline with sodium carbonate, and any ammonia produced estimated by the aëration method of Folin. Acetamide gave 26·2, propionamide 26·3, asparagine 4·9%. Formamide was apparently completely hydrolysed with the formation of 96·2% of ammonia.

If the reaction of amino-acids with nitrous acid in acetic acid solution is taken as an indication of the presence of a primary amino-group, the difference in the behaviour of amides should be represented by giving amides the alternative formula, R·C(OH):NH, which may be regarded as being converted in the presence of mineral acid into the more usual formula, $R{\cdot}CO{\cdot}NH_2$, which shows the presence of an $-NH_2$ group. This alternative formula is supported by the formation of unstable salts of amides, which are decomposed by water.

Urea and Derivatives.—Van Slyke has stated that urea reacted slowly with nitrous acid in the presence of acetic acid. These results show that at low temperatures (from 10° to 12°) the reaction is not complete, but that complete decomposition occurs at 18° to 20°. Werner, under different experimental conditions, did not observe complete reaction, and attributed the incompleteness to the formation of ammonium salts. As seen from the experiment with ammonium acetate, it is completely decomposed in 24 hours. The difference in the results seems to be due to the length of time of the reaction. As urea was decomposed in the presence of acetic acid, no experiments were made in the presence of hydrochloric acid.

On comparing the results with those of amides, it appears that urea possesses the alternative formula, $HN{=}C{<}^{O}_{NH_2}$ which changes in presence of acids to $HN{=}C{<}^{OH}_{NH_2}$, as proposed by Werner. The substance with the latter formula showing an $-NH_2$ group would be attacked by nitrous acid; *iso*cyanic acid, which is easily hydrolysed to ammonium carbonate, would also yield nitrogen.

This alternative formula for urea is supported by the behaviour of semicarbazide and urethane. One-third of the nitrogen of semicarbazide was obtained as gas in the presence of acetic acid, rather more in the presence of 2 or 3 c.c. of hydrochloric acid. One of the three nitrogen atoms would thus be present as an $-H_2N$ group. In presence of more hydrochloric acid, large volumes of gas were evolved, suggesting that hydrazine was formed by decomposition. Hydrazine in another experiment was observed to produce large

volumes of gas, probably resulting from reduction of nitrous acid by hydrazine.

Urethane behaved like the simple amides: no evolution of nitrogen in presence of acetic acid, but complete reaction in presence of hydrochloric acid. It would thus appear to have the alternative formula, $OEt{\cdot}C(OH){:}NH$, which changes into $OEt{\cdot}CO{\cdot}NH_2$ in presence of mineral acid.

The behaviour of biuret with nitrous acid is most easily explained by Werner's formula, $NH{:}C(OH){\cdot}NH{\cdot}C(OH){:}NH$. In presence of acetic acid, this would change to $NH{:}C(OH){\cdot}NH{\cdot}CO{\cdot}NH_2$ with liberation of one-third of its nitrogen as gas, as found by experiment; in the presence of 2 to 3 c.c. of hydrochloric acid, the formula would become $NH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$; two-thirds of the nitrogen was given off. In presence of 4 to 6 c.c. of hydrochloric acid, the whole of the nitrogen was evolved, indicating that the molecule was completely broken down.

Guanidine and Derivatives.—Guanidine reacted only slightly in presence of acetic acid, two-thirds of its nitrogen was given off in presence of 5 c.c. of hydrochloric acid, and the reaction was nearly complete in presence of 8 c.c. of hydrochloric acid in 23 hours.

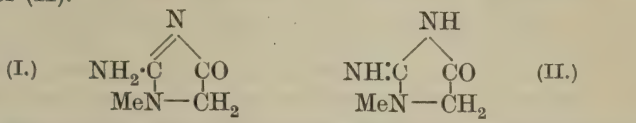
The alternative formula, $HN{=}C\begin{smallmatrix}NH_3\\|\\NH\end{smallmatrix}$, proposed by Krall, is indicated for guanidine. This changes to the usually adopted formula, $NH{:}C(NH_2)_2$, in presence of mineral acid, which explains the liberation of two-thirds of its nitrogen in presence of hydrochloric acid.

Arginine behaved in a similar way to guanidine. Only the α-amino-group reacts with nitrous acid in presence of acetic acid. This reaction is used in its analysis. An excess of nitrogen over one-third was found by Plimmer (*Biochem. J.*, 1924, **18**, 105) if the reaction were prolonged. The whole of its nitrogen is given off as gas in the presence of hydrochloric acid.

Aminoguanidine gave off one-quarter of its nitrogen as gas in presence of acetic acid, but larger quantities in presence of hydrochloric acid. Corresponding with guanidine, the whole of the nitrogen was not evolved as gas.

Creatine reacted in a similar way to guanidine and appears to have an alternative formula such as $CO_2H{\cdot}CH_2{\cdot}NMe{\cdot}C\begin{smallmatrix}NH_3\\|\\N\end{smallmatrix}$, which changes to the usual formula, $CO_2H{\cdot}CH_2{\cdot}NMe{\cdot}C(:NH){\cdot}NH_2$, in presence of hydrochloric acid. A volume of nitrogen was evolved corresponding to two nitrogen atoms. The third nitrogen atom, to which the methyl group is attached, would not be expected to yield nitrogen. Creatinine, which was also found by Wright Wilson to

react with nitrous acid in presence of acetic acid, showed an unexpected behaviour, indicating the presence of an amino-group. It would thus appear to have an alternative formula such as (I) instead of (II).



The effect of mineral acid in diminishing the volume of nitrogen evolved may be due to a change of the new alternative formula to the commonly adopted one. The formation of the smaller amounts of nitrogen in the experiments may be due to the method of adding the hydrochloric acid, 1 c.c. at a time; a certain volume would be liberated before the whole of the 6 or 8 c.c. could be introduced.

Summary.

1. Amides and urethane do not react with nitrous acid in presence of acetic acid.

2. Both react quantitatively in presence of approximately 2*N*-hydrochloric acid.

3. Urea reacts quantitatively with nitrous acid in presence of acetic acid.

4. Biuret reacts with one nitrogen atom in presence of acetic acid, with two nitrogen atoms in presence of small amounts of hydrochloric acid, with three nitrogen atoms in presence of 2*N*-hydrochloric acid.

5. Guanidine and creatine do not react with nitrous acid in presence of acetic acid, but give off nitrogen in presence of hydrochloric acid.

Arginine, excepting its primary α-amino-group, behaves in a similar way.

6. Creatinine gives off nitrogen corresponding to one nitrogen atom with nitrous acid in presence of acetic acid; the volume of nitrogen evolved is diminished in presence of hydrochloric acid.

7. If nitrous acid in presence of acetic acid is a reagent for the presence of an $-NH_2$ group, amides and the other compounds investigated will possess alternative formulæ, which, in presence of hydrochloric acid, change to the usually accepted formulæ for these compounds.

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CCCLXIII.—*Solubility Influences. Part I. The Effect of some Salts, Sugars, and Temperature on the Solubility of Ethyl Acetate in Water.*

By Samuel Glasstone and Albert Pound.

Although much work has been done on the influence of salts on the solubility in water of various non-electrolytes (for chief references, see Eyre, *Brit. Assoc. Rep.*, 1910, 447; 1912, 820; Rivett and Rosenblum, *Trans. Faraday Soc.*, 1914, **9**, 297; Linderström-Lang, *Compt. Rend. Trav. Lab. Carlsberg*, 1924, **15**, No. 4), there seems to have been very little attempt made at a systematic investigation. Very little work, too, has been done on the influence of non-electrolytes such as sugars on the solubility of other non-electrolytes such as ethyl acetate, ether, and aniline, and, as far as the present author is aware, there has been no systematic investigation of the effect of a mixture of substances, either electrolytes or non-electrolytes, on the solubility of a sparingly soluble, neutral substance. It seemed very probable that a complete examination of the so-called "salting out" effect would throw some light on the larger problem of solution, and the work described below was intended to be a contribution towards a more systematic survey of the problem than has yet been made.

In the present work, the solubility of ethyl acetate has been determined at 25° and at 50° in pure water and in the presence of various sugars and of the chlorides, bromides, and iodides of the alkali metals and of ammonium. Some rough measurements have also been made of the solubility of various salts in ethyl acetate saturated with water (about 3%), and an interesting qualitative connexion between these values and those of the solubility of ethyl acetate in salt solutions has been established. The solubility of ethyl acetate in water has also been determined at 0°, 10°, and 37°.

Philip (J., 1907, **91**, 711) has shown the advantage of expressing solubility results of this kind in terms of grams or gram-moles per 1000 grams of solvent rather than per litre of solution. A further change is now made, the results being expressed in terms of the number of gram-mols. of water required to dissolve one gram-mol. of ethyl acetate in the presence of various molecular quantities of added sugar or salt; in this form the results are useful for various calculations and for comparison with one another.

Experimental.

Ethyl acetate made by Roberts's method (*J. Soc. Chem. Ind.*, 1924, **43**, 295T) was purified from alcohol by distillation over calcium chloride and then by several fractionations over phos-

phorus pentoxide; only the final constant-boiling fraction was used in this work. The salts and sugars were the purest commercial specimens, mainly supplied by the British Drug Houses, Ltd., and no attempt was made to purify them; slight impurities had very little effect on the solubility of ethyl acetate, and this was probably less than the experimental error. The various solutions were made up by careful weighing of the substance and the water, and were saturated with ethyl acetate as follows: Since the solubility of ethyl acetate in water and in aqueous solutions decreases with rise of temperature (see below), the solution was shaken with a slight excess of the ester at a temperature below 25° or 50° and placed in a thermostat at 25° or 50°; the excess of ethyl acetate then separating caused the liquid to become cloudy. In the course of an hour or two the aqueous liquid was clear again, and was a saturated solution of the ester at the temperature of the thermostat. Care was always taken that the excess of ethyl acetate present was not so large that the amount of water or salt dissolved by it could not be neglected.

For analysis, a quantity of the saturated solution (3 to 8 g., depending on the ester concentration) was transferred rapidly in a warmed pipette to a stoppered bottle and weighed; care was taken that none of the acetate layer was drawn into the pipette. In the cases of the various salts which it was desired to recover, and of the sugars, the weighed solution was diluted with water, washed into a distilling flask, and the ethyl acetate, and some water, distilled over and collected in water in such a way as to avoid loss of ester. The residue in the flask was always tested to make sure that no acetic acid, which might have resulted from the hydrolysis of the ester by boiling water, remained behind. The ester was then hydrolysed with standard sodium hydroxide and estimated in the usual way. When the original solution contained an ammonium salt, distillation was always necessary, and in case the salt had become hydrolysed during this process and ammonia distilled over, the solution, after alkali hydrolysis, was boiled for a few minutes without the reflux condenser in order to expel ammonia. If distillation was unnecessary, the weighed solution was diluted and hydrolysed directly.

Results.—The columns headed m and w give the number of g.-mols. of added substances and of water, respectively, required to make a solution which will be saturated with 1 g.-mol. of ethyl acetate at the temperature stated. The significance of the figures in the column headed n is explained on p. 2664. In the absence of any added substance the value of w (w_0) is 66·15 at 25° and 80·98 at 50°.

Lithium chloride.			Lithium bromide.			Lithium iodide.		
m.	*w.*	*n.*	*m.*	*w.*	*n.*	*m.*	*w.*	*n.*
				25°.				
0·667	76·67	15·7	0·287	68·16	7·0	0·475	*65·90*	—
2·27	98·92	14·5	0·777	71·19	6·4	0·905	*62·60*	—
6·28	133·7	10·7	1·824	77·14	6·0	1·957	*58·40*	—
24·85	231·5	6·7	4·85	91·19	5·2	3·44	*38·5*	—
134·5	476·2	3·3	13·26	96·27	2·3			
			15·66	*40·65*	—			
				50°.				
0·858	98·65	20·6	0·354	84·03	8·6	0·566	*78·5*	—
2·905	125·9	15·0	0·935	85·47	4·8	1·112	*76·9*	—
8·08	171·8	11·2	2·325	98·46	7·5	2·36	*70·5*	—
31·55	294·1	6·7	6·12	115·2	5·6	5·02	*56·0*	—
181·2	641·0	3·1	18·40	133·3	2·9	0·912	*4·56*	—
			19·58	*83·5*	—			

Sodium chloride.			Sodium bromide.			Sodium iodide.		
				25°.				
0·219	70·68	20·7	0·229	71·10	—	0·163	67·14	6·7
0·477	76·65	22·0	0·630	76·76	16·8	0·432	68·25	4·8
1·540	94·34	18·3	1·560	87·72	13·9	0·774	68·78	3·5
4·86	142·0	15·6	4·91	121·2	11·2	2·165	73·37	3·3
12·03	218·8	12·7	12·10	173·3	8·8	6·46	82·58	2·5
27·10	352·1	10·6	47·40	367·6	6·4	21·32	109·4	2·0
59·30	581·4	8·7						
				50°.				
0·273	88·12	26·1	0·294	91·66	—	0·243	84·37	13·6
0·589	94·80	23·4	0·794	96·64	19·6	0·535	84·75	7·0
2·02	123·5	21·0	2·69	116·3	13·1	0·978	86·58	5·6
6·43	188·0	16·6	6·43	158·7	12·1	2·81	95·24	5·0
14·40	261·8	12·6	15·48	221·7	9·1	8·44	107·8	3·2
33·42	434·8	10·6	52·60	408·2	6·2	27·76	142·5	2·2
85·00	833·3	8·9						

Potassium chloride.			Potassium bromide.			Potassium iodide.		
				25°.				
0·168	69·15	17·8	0·249	69·20	12·3	0·150	68·03	12·5
0·369	74·75	23·3	0·610	76·70	17·3	0·395	69·69	9·0
1·093	86·21	18·3	1·39	84·03	12·8	0·860	71·43	6·1
3·06	112·9	15·2	4·29	114·9	11·3	2·02	75·19	4·5
6·96	155·0	12·7	9·44	148·6	8·7	6·45	87·72	3·3
12·19	203·7	11·3	21·90	220·8	7·0	20·19	125·0	2·9
22·90	284·9	9·5						
				50°.				
0·213	87·57	—	0·370	85·09	11·0	0·181	82·26	7·0
0·458	92·73	25·5	0·737	92·59	15·7	0·473	83·33	4·9
1·438	113·3	22·4	1·774	107·1	14·7	1·045	86·81	5·5
4·09	152·7	17·5	5·46	146·0	11·9	2·44	90·91	4·1
8·87	197·6	13·1	12·65	199·2	9·3	7·71	106·7	3·3
14·70	245·7	11·2	30·68	308·6	7·4	24·22	149·9	2·8
31·07	386·1	9·8						

Rubidium chloride.			Rubidium bromide.			Rubidium iodide.		
				25°.				
0·578	77·52	19·7	0·421	73·53	17·5	0·298	66·82	2·2
1·454	93·10	18·5	0·993	80·65	14·5	0·635	68·78	4·1
5·22	135·9	13·3	2·55	94·69	11·2	1·475	69·69	2·4
14·20	224·7	12·5	7·65	132·5	8·6	2·66	73·42	2·7
67·8	546·4	7·1	24·00	222·7	6·5	5·69	82·58	2·9
						12·53	107·0	3·2

Rubidium chloride.			Rubidium bromide.			Rubidium iodide.		
m.	*w.*	*n.*	*m.*	*w.*	*n.*	*m.*	*w.*	*n.*
				50°.				
0·742	94·5	18·2	0·502	87·64	13·2	0·358	80·33	—
6·62	172·4	13·8	3·23	119·8	12·0	1·788	84·37	1·9
84·4	680·3	7·1	40·5	375·9	7·2	7·26	105·3	3·3

Cæsium chloride.			Cæsium bromide.			Cæsium iodide.		
				25°.				
0·427	74·52	19·6	0·321	70·68	14·1	0·237	67·79	6·9
1·004	86·21	20·0	0·693	74·52	12·1	0·538	68·87	5·1
3·065	113·6	15·5	1·835	86·81	11·2	1·241	70·78	3·7
7·04	153·1	12·4	3·47	97·95	9·1	2·70	72·30	2·3
26·70	294·1	8·5	8·80	135·0	7·8			
132·5	671·1	4·6						
				50°.				
0·530	92·59	21·9	0·400	88·12	17·8	0·290	82·88	6·5
3·802	141·0	15·7	2·235	105·8	11·1	1·487	84·79	2·6
29·95	330·0	8·3	11·92	179·9	8·3	3·44	93·01	3·5
197·8	1000·0	4·6	35·10	275·5	5·5			

Ammonium chloride.			Ammonium bromide.			Ammonium iodide.		
				25°.				
0·525	76·54	19·8	0·273	70·0	13·6	0·422	*64·4*	—
1·568	89·14	14·7	0·725	74·4	11·4	0·866	*63·2*	—
4·28	112·4	10·8	1·680	81·9	9·4	1·87	*60·8*	—
8·41	139·7	8·7	4·33	94·0	6·4	4·74	*57·4*	—
14·95	174·5	7·2	8·55	109·5	5·1	12·42	*62·1*	—
			16·38	122·7	3·5			
				50°.				
0·632	92·14	17·6	0·338	86·5	16·2	0·513	*80·4*	—
1·973	112·2	15·8	0·839	90·8	11·7	1·094	*79·6*	—
5·65	148·4	11·9	2·107	102·5	10·2	2·418	*78·7*	—
11·42	189·8	9·4	5·55	120·6	7·1	6·28	*76·2*	—
18·61	216·9	7·8	11·77	150·8	5·9	16·32	88·8	0·5
			21·78	177·0	4·4			

Dextrose.			Lævulose.			Sucrose.		
				25°.				
0·0692	68·6	25·4	0·394	73·8	19·4	0·0734	66·4	
0·1423	69·3	22·0	0·867	78·3	14·0	0·190	68·5	12·9
0·392	73·6	19·0	1·445	81·9	10·9	0·406	69·6	8·5
0·871	78·6	14·3	2·178	87·0	9·6	0·696	75·0	12·7
1·486	84·1	12·1	4·270	99·8	7·9	1·010	77·6	11·3
2·262	90·6	10·8	8·65	131·0	7·5	1·935	86·7	10·6
3·315	98·5	9·7				3·57	101·5	9·9
						6·10	115·9	8·1
				50°.				
0·0826	81·8	9·7	0·475	89·0	16·6	0·091	82·1	12·1
0·1708	83·1	12·3	1·045	94·3	12·7	0·233	83·9	12·4
0·462	86·6	12·1	1·720	97·4	9·5	0·508	87·0	11·8
1·016	91·5	10·3	2·520	101·0	7·9	0·833	89·6	10·3
1·705	96·6	9·1	4·76	111·2	6·3	1·206	92·9	9·9
2·593	103·6	8·7	8·89	134·6	6·1	2·35	105·4	10·4
3·722	110·7	8·0				4·18	119·0	9·1
						6·81	129·2	7·1

Lactose.

25°.			50°.		
m.	*w.*	*n.*	*m.*	*w.*	*n.*
0·0706	69·4	46·0	0·0848	83·3	27·1
0·190	72·5	33·4	0·222	84·7	16·7
0·423	77·4	26·6	0·487	89·0	16·4
0·739	82·0	21·4	0·854	94·8	16·2
1·094	88·7	20·6	1·234	100·0	15·6
1·575	94·7	18·1	1·762	105·9	14·1

Discussion.

In general, the effect of one substance in reducing the solubility of another has been explained along two different lines. Euler (*Z. physikal. Chem.*, 1899, **31**, 360) suggested that the addition of a salt to water increases the internal pressure, and this results in a decreased solvent power for a neutral solute; this theory was supported by Geffcken (*ibid.*, 1904, **49**, 257), but was adversely criticised by Levin (*ibid.*, 1906, **55**, 503). On the other hand, Rothmund (*ibid.*, 1900, **33**, 401) suggested that the reduction in solubility is due to the added salt becoming hydrated in solution, so that the molecules of water involved in the hydration are no longer available for the dissolution of another substance. Although Rothmund later criticised this point of view (*ibid.*, 1909, **69**, 523), it received support from Baur (Ahren's *Sammlung*, 1903, **8**, 466), Lowry (*Trans. Faraday Soc.*, 1905, **1**, 197) and Philip (J., 1907, **91**, 711). The last author was the first to make use of solubility determinations in salt solutions in order to calculate the hydration values of various salts; by assuming that the reduction in solubility of the neutral substance is entirely due to the water molecules removed in the salt-hydrate, average values for the number of molecules of hydrate water per molecule of salt can be obtained. Philip's method of calculating hydration values has been applied to the results obtained in the present work, and the average degree of hydration of the salts, etc., at various concentrations, which is equal to $(w - w_0)/m$, is given in the column headed *n*.

Since there is some doubt as to the condition of molecules and ions in concentrated solutions, the hydration values for different salts are best compared at infinite dilution; consequently all the hydration numbers obtained above have been extrapolated roughly to zero concentration. The results are given below; as the values do not vary appreciably between 25° and 50°, average results are recorded.

Hydration of Salts at Infinite Dilution.

LiCl ... 27	NaCl ... 24	KCl ... 22	NH_4Cl ... 21	RbCl ... 20	CsCl ... 20
LiBr ... 9 ?	NaBr ... 19	KBr ... 17	NH_4Br ... 16	RbBr ... 16	CsBr ... 15
LiI ... ?	NaI ... 14 ?	KI ... 12 ?	NH_4I ... ?	RbI ... 5 ?	CsI ... 8 ?

The results for the lithium salts and almost all the iodides are uncertain; the solubility figures in italics (pp. 2662—3) show that lithium bromide at the highest concentrations, and lithium and ammonium iodides at almost all concentrations, increase the solubility of ethyl acetate in water. The increase is probably connected with the formation of a compound between the salt and the ester; concentrated solutions of iodides containing ethyl acetate have a distinct yellow colour which is not due to the presence of free iodine and can be attributed only to the presence of some complex substance in solution. There was no evidence of a metathetical reaction between the salt and the ester. The remarkable fact that at 25° ethyl acetate and a 60% solution of lithium iodide in water are miscible in all proportions merits further investigation. Some experiments have been made on the solubility of the various salts in ethyl acetate saturated with water; lithium chloride, sodium, potassium, ammonium, rubidium and cæsium iodides are slightly soluble, whilst lithium bromide and iodide are considerably soluble (roughly 30% and 40%, respectively, at 25°). It is with the salts which are soluble in ethyl acetate, therefore, that anomalous results have been obtained; it follows, then, that whenever the added salt either combines with or is soluble in the neutral solute the hydration values calculated by the method described above are useless.

Although the hydration values given above are in good agreement with those calculated by other authors from a variety of solubility measurements (Philip, *loc. cit.*; Philip and Bramley, J., 1915, **107**, 377; McArthur, *J. Physical Chem.*, 1916, **20**, 495; Thorne, J., 1921, **119**, 262; Manchot, Jahrstorfer, and Zepter, *Z. anorg. Chem.*, 1924, **141**, 45), it does not follow that hydration is the main, or even the subsidiary, cause of salting-out. This effect may be due to some other fundamental property of each ion or molecule, which is independent of the nature of the substance being salted-out, provided no compound formation occurs. In the case of the sugars, some of the hydration values calculated by the method described above appear to be incredibly large and to vary considerably with temperature, and so it is probable that other factors are operative.

It is seen also that molecules of a non-electrolyte have the power of reducing very considerably the solubility of ethyl acetate in water. Euler and his co-workers (*Z. Elektrochem.*, 1917, **23**, 192; *Z. physiol. Chem.*, 1924, **140**, 113) appear to have tacitly assumed that only *ions* are responsible for salting-out, but it is clear that this assumption is not justifiable. McKeown also (*J. Amer. Chem. Soc.*, 1922, **44**, 1203), in attempting to assess the salting-out powers

of sodium- and chlorine-ions, assumes that the salting-out effect of undissociated molecules is very small; he finds that when ether is salted out with sodium chloride the effect is entirely due to the chlorine ions. It should be pointed out, however, that since the equations from which this result is obtained are admittedly approximate, the conclusion is of little value; almost equally good agreement with most of the equations may be obtained by using entirely different values from those of McKeown. In the case of ethyl acetate, it is clear that both anions and kations have definite salting-out power; the kations would be placed in the order $Li > Na > K > NH_4 > Rb > Cs$, and the anions in the order $Cl > Br > I$.

Various authors have attempted to obtain equations which connect the solubility of a neutral substance in a salt, or other, solution with the concentration of added salt; in general, an equation of the type $\log s = a - kc$ has been found to be most satisfactory, where s is the solubility of the neutral substance, c the concentration of salt, and a and k are constants (for references, see Thorne, *loc. cit.*, and Linderström-Lang, *loc. cit.*). In the present work, it has not been possible to find any one equation which will fit all the results up to the highest concentrations of added salt; in general, the logarithmic equation was found to hold good in the form $\log w = km/w + a$, where a and k are constants for a given salt, and w and m have the same meaning as before, up to concentrations of $2—3N$. For some salts—sodium, potassium, and rubidium chlorides—the agreement was very good almost up to the saturation point. In those cases in which the salt was soluble in ethyl acetate the logarithmic equation was not obeyed at all. In the presence of lithium chloride, the solubility of ethyl acetate may be expressed by the straight-line equation $w = km + a$, and a similar equation holds good for the more concentrated sugar solutions. The fact that the results will not all conform to one simple equation suggests that the salting-out effect is due to several different factors, on which, it is hoped, further investigations will throw light.

Solubility of Ethyl Acetate in Water.

As the literature is very deficient in measurements of the solubility of ethyl acetate in water at different temperatures, a number of determinations have been made by the method described above for salt solutions, with the following results :—

Grams of Ethyl Acetate dissolved by 100 grams of Water.

10·40 at 0°; 8·96 at 10°; 7·39 at 25°; 6·65 at 37°; 6·04 at 50°.

The following figures have been obtained by interpolation from a graph :—

7·85 at 20°; 7·06 at 30°; 6·50 at 40°.

The solubility thus decreases steadily as the temperature is raised from 0° to 50°.

Summary.

(1) The solubility of ethyl acetate has been determined at 25° and 50° in solutions of the chloride, bromide, and iodide of the alkali metals and of ammonium, and in solutions of dextrose, lævulose, sucrose, and lactose.

(2) It is shown that hydration of the salt may be one of the factors responsible for the salting-out effect; this effect may, however, be due to some other fundamental property of salt ions or molecules. Molecules, as well as ions, probably have considerable salting-out power.

(3) The solubility of ethyl acetate in salt solutions is best expressed by a logarithmic equation, *e.g.*, $\log w = km/w + a$; the application of this equation, however, is limited to the more dilute salt solutions.

(4) The solubility of ethyl acetate in water has been determined at 0°, 10°, 25°, 37°, and 50°; the solubility decreases with increasing temperature.

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CCCLXIV.—*The Preparation of Tertiary Arsines by the Friedel-Crafts Reaction.*

By Arthur Frederick Hunt and Eustace Ebenezer Turner.

The first successful application of the Friedel-Crafts reaction to the preparation of tertiary arsines was the conversion of phenylmethylchloroarsine into diphenylmethylarsine (Burrows and Turner, J., 1921, **119**, 426). If the reaction were generally applicable to the preparation of tertiary arsines, cases would arise where it would be preferable to syntheses involving the use of the Grignard reagent. A few examples have been studied, and it has been found that phenylmethylchloroarsine (chosen because of its ready accessibility) condenses with mesitylene to give *phenylmesitylmethylarsine*, and with toluene and bromobenzene to give mainly the para-compounds,

phenyl-p-*tolylmethylarsine* and p-*bromodiphenylmethylarsine*, respectively. Proof of the constitution of the two last-named compounds has been obtained by independent syntheses, using the usual methods. In other Friedel-Crafts reactions, bromobenzene gives mainly para-compounds (Dilthey, *J. pr. Chem.*, 1925, **109**, 273).

It appears to be advisable, in the case of Friedel-Crafts reactions with arsenic compounds, to use an excess of the non-arsenical component, and to remove the hydrogen chloride as fast as it is formed by keeping the reaction mixture gently boiling under diminished pressure. In the reaction with bromobenzene, a little of the latter is converted into 4-bromodiphenyl.

Experimental.

Preparation of Phenylmethylchloroarsine.—The substitution of methyl chloride and sulphate for methyl iodide in the methylation of phenylarsenious oxide (Burrows and Turner, *loc. cit.*) gave unsatisfactory results (yields of phenylmethylchloroarsine, 56% and 55%, respectively).

Preparation of Phenyl-p-*tolylmethylarsine.*—(a) *From phenylmethylchloroarsine and toluene.* To a mixture of 15 g. of phenylmethylchloroarsine and 60 g. of toluene were added 15 g. of powdered anhydrous aluminium chloride, and the resulting red solution was heated under reflux for 2·5 hours; evolution of hydrogen chloride had then almost ceased. The dark-coloured product was poured on to a mixture of ice and hydrochloric acid, when a brownish-red precipitate and a green, fluorescent oil separated. The oil was removed and filtered, washed with sodium hydroxide to remove unchanged chloroarsine, dried over anhydrous sodium sulphate, and freed from toluene by distillation. The residue, when distilled under diminished pressure, gave 8 g. of *phenyl*-p-*tolylmethylarsine* (see below), an almost colourless liquid, b. p. 164—165°/12 mm. (Found: As, 29·1. $C_{14}H_{15}As$ requires As, 29·1%). The arsine has an unpleasant fishy odour, and slowly oxidises on keeping, with gradual separation of colourless crystals. It combines with methyl iodide slowly at the ordinary temperature (2 to 3 weeks), and rapidly at 100°, with production of *phenyl*-p-*tolyldimethylarsonium iodide*, colourless prisms, m. p. 93° (Found: I, 31·7. $C_{15}H_{18}IAs$ requires I, 31·8%).

Phenyl-*p*-tolylmethylarsine combines readily with ethyl iodide at 100° to give the phenyl-*p*-tolylmethylethylarsonium iodide obtained by Michaelis (*Annalen*, 1902, **321**, 160) from phenyl-*p*-tolylethylarsine and methyl iodide. The iodide was described by Michaelis as melting at 145° or at 150—151° when crystallised from alcohol, or from water, respectively. The compound has now

been found to melt at 150° when crystallised from alcohol, and at 158° when crystallised from water. Once it had been crystallised from water, recrystallisation from either solvent did not affect the m. p. (158°) (Found : I, 30·6. Calc., I, 30·7%).

Phenyl-*p*-tolylmethylarsine forms with mercuric chloride a white, crystalline *additive* compound, which may be crystallised from glacial acetic acid.

(b) *From magnesium* p-*tolyl iodide and phenylmethylchloroarsine.* A Grignard reagent made from 24 g. of *p*-iodotoluene, 2·6 g. of magnesium, and 100 c.c. of ether was slowly treated with 20·4 g. of phenylmethylchloroarsine dissolved in 20 c.c. of ether. When the initial reaction was over, the whole was heated under reflux for 2 hours, and worked up in the usual manner. In this way, 18 g. (76% yield) of phenyl-*p*-tolylmethylarsine were obtained, b. p. 167°/14 mm. The odour of this sample was less pronounced than that of the sample from (a), but both substances otherwise possessed similar properties. The arsine from (b) gave the same methiodide (m. p. 92°) as that from (a), a mixture of the two methiodides melting at 92°.

Preparation of Phenylmesitylmethylarsine.—A mixture of 15 g. of phenylmethylchloroarsine and 35 g. of mesitylene, treated with 15 g. of aluminium chloride, became slightly warm and turned red. It was boiled gently under reflux at 75—80°/45 mm. for some hours; when the evolution of hydrogen chloride slackened, the product was poured on to a mixture of ice and hydrochloric acid. The resulting oil was extracted with benzene, the extract filtered from a reddish-brown precipitate, shaken with alkali, and worked up in the normal manner; 15 g. of mesitylene and 7 g. of *phenylmesitylmethylarsine* (yield 30%) were obtained. The latter is a colourless, mobile liquid having a faint fishy odour, oxidises slowly in the air to give a white, crystalline solid, and boils at 164°/17 mm. (Found : As, 26·6. $C_{16}H_{19}As$ requires As, 26·2%).

The arsine combines readily with methyl iodide at 100° to give *phenylmesityldimethylarsonium iodide*, which is moderately soluble in alcohol, and separates from that solvent in colourless prisms, m. p. 187° (Found : I, 29·6. $C_{17}H_{22}IAs$ requires As, 29·7%).

The arsine combines with benzyl bromide slowly at the ordinary temperature, and rapidly at 100° to give *phenylmesitylbenzylmethylarsonium bromide*, which crystallises from alcohol, or better, from water, in colourless prisms, m. p. 179—180° (Found : Br, 17·7. $C_{23}H_{20}BrAs$ requires Br, 17·5%).

Preparation of p-*Bromodiphenylmethylarsine.*—(a) *From phenylmethylchloroarsine and bromobenzene.* A mixture of 20 g. of the chloroarsine, 60 g. of bromobenzene, and 20 g. of aluminium chloride

was kept briskly boiling under diminished pressure (bath at about 35°). After an hour, when the evolution of hydrogen chloride had almost ceased, the cooled product was poured on to ice and hydrochloric acid, and was worked up in the usual manner. On distillation, 35 g. of bromobenzene were recovered. At 140—160°/15 mm., 2 g. of 4-bromodiphenyl distilled (white plates, m. p. 81°. Found : Br, 33·9. Calc., Br, 34·3%). At 170—200°/15 mm., 5 g. of p-*bromodiphenylmethylarsine* (see below) distilled as a colourless liquid (Found : As, 23·6. $C_{13}H_{12}BrAs$ requires As, 23·2%).

The arsine combined readily with methyl iodide in a closed tube at 100° to give a crystalline product which could not be recrystallised from the usual solvents. The combination of the arsine with methyl iodide in the cold (2 to 3 weeks), however, gave p-*bromodiphenyldimethylarsonium iodide*. This was precipitated by absolute ether from its solution in absolute alcohol, and formed very pale yellow prisms, m. p. 87° (Found : I, 27·0. $C_{14}H_{15}BrIAs$ requires I, 27·3%).

The *benzobromide* of *p*-bromodiphenylmethylarsine was obtained as a colourless viscid mass which could not be crystallised.

(b) *From* p-*bromophenylmethyliodoarsine*. *p*-Bromophenylarsinic acid was prepared from *p*-bromoaniline in the usual manner, and reduced with hydrochloric–hydriodic–sulphurous acid, when p-*bromophenyldichloroarsine* was obtained. The crude, red dichloroarsine, when treated with sodium carbonate in presence of warm water, gave p-*bromophenylarsenious oxide* as a sticky yellow solid. It was purified by dissolving in alcohol and precipitating with water, and then formed white prisms, m. p. 259—261° (Found : As, 30·7. C_6H_4OBrAs requires As, 30·4%). The oxide may be methylated direct, but as some pure dichloroarsine was required for another purpose, the oxide was converted into the latter in the usual manner. *p*-Bromophenyldichloroarsine was thus obtained as a heavy, orange-coloured liquid, boiling at 164°/18 mm., and having physiological properties similar to those of phenyldichloroarsine (Found : Cl, 23·5. $C_6H_4Cl_2BrAs$ requires Cl, 23·5%).

The dichloroarsine (30·2 g.) and 16 g. of sodium hydroxide were dissolved in a mixture of 200 c.c. of water and 200 c.c. of alcohol, 16 g. of methyl iodide were added, and the mixture was left for 12 hours. Concentrated hydrochloric acid (500 c.c.) and a little potassium iodide were added, and the solution was saturated with sulphur dioxide. The dark-coloured oil which separated was dried over sodium sulphate, and distilled under diminished pressure, when 25 g. (70% yield) of p-*bromophenylmethyliodoarsine* were obtained, b. p. 178—180°/23 mm. The iodoarsine became solid on cooling, and formed pale yellow needles, m. p. 36·5° (Found : I, 34·1. C_7H_7BrIAs requires I, 34·0%).

A Grignard reagent was prepared from 12 g. of bromobenzene, 24 g. of magnesium, and 250 c.c. of ether, and a solution of 24 g. of the iodoarsine was slowly added, a vigorous reaction occurring. The mixture was heated under reflux for 0·5 hour, and decomposed in the usual manner. The ethereal extract was shaken with alkali before being dried over sodium sulphate. *p*-Bromodiphenylmethylarsine (12 g., 60% yield) was finally obtained, having properties similar to those of the product of the Friedel-Crafts reaction. Identity of the two products was established through the methiodides, which did not depress each other's m.p.

During the course of this work, the following compounds were prepared incidentally :

p-*Chlorophenyldichloroarsine*, a colourless, highly refractive liquid, b. p. 277° or at 160°/23 mm. [Found : Cl (attached to arsenic), 27·5. C_6H_4ClAs requires Cl, 27·6%]. p-*Chlorophenylarsenious oxide*, which crystallises from benzene in white needles, m. p. 198° (Found : As, 36·4. C_6H_4OClAs requires As, 37·0%). *Di*-p-*chlorophenylchloroarsine*, a pale yellow solid, m. p. 51° (Found : Cl, 31·8. $C_{12}H_8Cl_3As$ requires Cl, 32·0%).

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CCCLXV.—$\gamma\gamma'$-*Dichlorodipropyl Sulphide.*

By GEORGE MACDONALD BENNETT and ALFRED LOUIS HOCK.

THE remarkable chemical reactivity of $\beta\beta'$-dichlorodiethyl sulphide must be attributed to the influence of the sulphur atom upon the two chlorine atoms. A high degree of reactivity is, in fact, generally shown by the chlorine atom in compounds of the general formula $R{\cdot}S{\cdot}CH_2{\cdot}CH_2Cl$, and there is a correspondingly high reactivity in the hydroxyl group of the parent compound, $R{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ (compare Bennett, J., 1922, **121**, 2140). The isomeric $\alpha\alpha'$-dichlorodiethyl sulphide (Bales and Nickelson, J., 1922, **121**, 2137; Mann and Pope, J., 1923, **123**, 1172) readily yields its chlorine when boiled in solution with alcoholic sodium hydroxide; the chlorine is therefore in a reactive condition. No data, however, are available for a quantitative comparison of the properties of chlorine atoms situated in the α- and β-positions.

$\gamma\gamma'$-*Dichlorodipropyl sulphide*, the first simple chlorosulphide

having the chlorine atom in the γ-position, has now been prepared. It is decidedly less reactive than ββ′-dichlorodiethyl sulphide and ββ′-dichlorodipropyl sulphide (Coffey, J., 1921, **119**, 94; Pope and Smith, *ibid.*, 396). It was prepared from *γγ′-dihydroxydipropyl sulphide* obtained by the action of sodium sulphide on γ-chloropropyl alcohol, but the replacement of the hydroxyl groups in the dihydroxy-sulphide by chlorine was as exceptionally difficult as the analogous reaction is surprisingly easy with β-hydroxy-sulphides. Whereas the latter operation is completed in a few minutes by boiling concentrated hydrochloric acid (Clarke, J., 1912, **101**, 1583; Coffey, *loc. cit.*), replacement of the hydroxyl groups of γγ′-dihydroxy-dipropyl sulphide did not occur when any of the usual reagents such as hydrochloric acid, phosphorus tri- or penta-chloride, or phosphorus tri-iodide were employed, and hydrogen chloride at 150° reacted only slowly to give a poor yield of chloro-compound. The hydroxyl groups in this sulphide are therefore less reactive than is usual in a primary alcohol. The use of thionyl chloride alone gave no better result, but the dichlorodipropyl sulphide was obtained easily in good yield when this reagent was used in presence of dimethylaniline (Darzens, *Compt. rend.*, 1911, **152**, 1314).

The difference in character of the β- and the γ-chlorine atoms is well shown by the action of potassium cyanide in alcoholic solution upon ββ′-dichlorodiethyl and γγ′-dichlorodipropyl sulphides. Whereas Davies has shown that the former is converted into an unexpected substance of the formula $C_6H_{12}S_2(CN)_2$ (J., 1920, **117**, 298), we find that the latter is smoothly converted into the dinitrile of thiodibutyric acid (Gabriel, *Ber.*, 1890, **23**, 2493).

A study of the oxidation of γγ′-dichlorodipropyl sulphide showed that the sulphur atom in the molecule has unusual properties. Although the action of sodium hypobromite, nitric acid, or hydrogen peroxide upon the sulphide at laboratory temperature might be expected to furnish a sulphoxide, these reagents produced the same compound which resulted from oxidation with chromic anhydride in boiling glacial acetic acid, namely, the *sulphone*,

$$SO_2(CH_2{\cdot}CH_2{\cdot}CH_2Cl)_2,$$

of m. p. 66°. It thus appears to be a property of the sulphide to take up two atoms of oxygen per molecule instead of one. Moreover, neither a sulphilimine nor a mercurichloride could be obtained from it, and its dibromide, which can be prepared only in the presence of a very large excess of bromine, is even more unstable than the dibromide of ββ′-dichlorodiethyl sulphide, so that there seems to be a general reluctance to form derivatives involving quadrivalency of the sulphur atom.

A comparison of the rates of reaction of ββ′-dichlorodiethyl and

$\gamma\gamma'$-dichlorodipropyl sulphides with sodium hydroxide in ethyl alcohol showed that, the course of the two reactions being assumed to be similar, the former reacts sixty times as fast as the latter. We hope to make a systematic comparison of these and other chlorosulphides when a synthesis of a δ-chloro-sulphide has been completed.

Experimental.

Action of Sodium Sulphide on γ-Chloropropyl Alcohol.—A solution of sodium sulphide (95 g. $Na_2S,9H_2O$) in an equal weight of water was added cautiously in three portions to γ-chloropropyl alcohol (60 g.), the mixture heated under reflux for 3 hours and then distilled with steam until the distillate no longer gave a white precipitate with mercuric chloride. The distillate was boiled with an excess of yellow mercuric oxide, filtered, concentrated, and cooled; a small quantity of the *mercaptide* of *γ-hydroxypropyl mercaptan*, $Hg(S\cdot C_3H_6\cdot OH)_2$, then separated out. It crystallised from *n*-butyl alcohol in silvery plates, m. p. 132—134° (Found: Hg, 52·9. $C_6H_{14}O_2S_2Hg$ requires Hg, 52·5%).

The solution remaining in the distillation flask was made acid with hydrochloric acid and concentrated on the steam-bath. The bulk of the sodium chloride was removed by filtration after dilution with acetone, the solution dried, and the acetone evaporated. The residual viscous oil was heated in a current of dry air at 100° under diminished pressure and finally poured off from a little sodium chloride which it deposited from solution.

$\gamma\gamma'$-Dihydroxydipropyl sulphide, $S(C_3H_6\cdot OH)_2$, was thus obtained as a viscous oil which could not be distilled or induced to crystallise, and was not analysed. With phenylcarbimide it reacted at once to give the *bisphenylurethane*, $S(C_3H_6\cdot O\cdot CO\cdot NHPh)_2$, colourless needles from benzene, m. p. 146—148° (Found: C, 62·1; H, 6·5. $C_{20}H_{24}O_4NS$ requires C, 61·8; H, 6·2%).

Action of Thionyl Chloride, Phosphorus Halides, and Hydrogen Chloride upon $\gamma\gamma'$-Dihydroxydipropyl Sulphide.—The dihydroxysulphide was not appreciably affected by heating for 2 hours with boiling concentrated hydrochloric acid. The action of thionyl chloride, phosphorus tri- or penta-chloride or phosphorus tri-iodide led to the production of non-volatile substances which were presumably esters of the corresponding hydroxy-acids. For example, after the dihydroxy-compound had reacted in presence of dry benzene with phosphorus tri-iodide (2/3 mol.), the material recovered from the solution could not be distilled under diminished pressure, and when kept in a desiccator it slowly hardened to a resinous mass without crystallising, an odour of mustard being simultaneously developed.

The replacement of the hydroxyl groups was first achieved as follows: the dihydroxypropyl sulphide was heated at 150—160° while a stream of dry hydrogen chloride was passed into it for 2·5 hours. The product was distilled; a small quantity of an oil, b. p. 135—150°/25 mm., was obtained, which consisted of practically pure dichlorodipropyl sulphide (yield 17%).

$\gamma\gamma'$-Dichlorodipropyl Sulphide.—Thionyl chloride (80 g.) was added drop by drop to a well-cooled mixture of $\gamma\gamma'$-dihydroxydipropyl sulphide (45 g.) and dimethylaniline (80 g.), kept below 60°. The mixture was then heated at 100° for ½ hour, poured into an excess of dilute hydrochloric acid, the oil extracted with chloroform, and the extract washed with water, dried, and distilled. *$\gamma\gamma'$-Dichlorodipropyl sulphide*, $S(C_3H_6Cl)_2$, was thus obtained as a faintly yellow oil of pronounced odour, b. p. 162°/43 mm. (yield 83%) (Found: C, 38·9; H, 6·5; Cl, 38·2; S, 16·7. $C_6H_{12}Cl_2S$ requires C, 38·5; H, 6·3; Cl, 37·9; S, 17·15%). The following constants were determined: $D_4^{20°}$ (vac.) = 1·175, $n_\alpha^{20°}$ = 1·5075, whence $[R_L]_\alpha$ = 47·42 (calc., 47·25). The liquid did not crystallise when cooled to the temperature of liquid air and allowed to revert slowly to normal temperature.

Compound with Platinic Chloride.—This was obtained in greenish-yellow plates, m. p. 83·5—85°, by adding platinic chloride (0·86 g.) in acetone to the chloro-sulphide (0·46 g.) also dissolved in acetone (5 c.c.), the product crystallising in the course of a few hours. It had the composition $2S(C_3H_6Cl)_2,PtCl_4$ (Found: Pt, 27·7. $C_{12}H_{24}Cl_8SPt$ requires Pt, 27·4%).

An unstable *dibromide*, $S(C_3H_6Cl)_2Br_2$, was obtained from the chloro-sulphide (0·94 g.) with bromine (4 g.) in carbon tetrachloride (5 c.c.). The crystals were quickly filtered off, washed with a little of the pure solvent, dried on porous tile, and analysed at once, since the substance decomposed completely when kept over-night (Found: Br, 57·7. $C_6H_{12}Cl_2Br_2S$ requires Br, 59·8%).

Repeated attempts to prepare a sulphilimine led only to the isolation of toluene-*p*-sulphonamide, m. p. 137° (Found: C, 48·8; H, 5·3. Calc., C, 49·1; H, 5·3%).

Action of Methyl Iodide.—When the chloro-sulphide was mixed with methyl iodide (5 mols.), crystals appeared in the liquid within ½ hour, of m. p. 179—181°, but a sufficient quantity for analysis could not be collected. If left in the liquid, the crystals soon redissolved and a viscous oil separated. This oil was almost entirely soluble in water, but the solution deposited an oil again on evaporation and dissociation of the sulphonium compound evidently took place with liberation of the original sulphide. The residue obtained by evaporating the excess of methyl iodide from the original mixture

could not be induced to solidify, but it readily combined with mercuric iodide to produce a solid which crystallised from acetone–chloroform in yellow needles (the chloro-sulphide itself is quite indifferent to mercuric iodide). After three recrystallisations, the substance had m. p. 84—88° and analysis showed it to be *dichlorodipropylmethylsulphonium mercuri-iodide*, $(C_3H_6Cl)_2SMeI,HgI_2$ (Found: Hg, 27·1; AgCl + AgI, 123·7. $C_7H_{15}Cl_2I_3SHg$ requires Hg, 25·65; AgCl + AgI, 126·5%). This compound was evidently not quite pure, but further purification was not possible, since dissociation of the substance occurred in solution, an odour of the original chloro-sulphide being always developed during recrystallisation.

Action of Oxidising Agents.—The chloro-sulphide was shaken with an ice-cold solution of sodium hypobromite (1·8 mols.), the mixture heated at 50° for 5 minutes, and finally cooled in ice; the oil obtained solidified to a mass of crystals, which were recrystallised from benzene–light petroleum. This substance was *$\gamma\gamma'$-dichlorodipropylsulphone*, $(C_3H_6Cl)_2SO_2$, m. p. 65—66° (Found: C, 32·7; H, 5·6; Cl, 32·4. $C_6H_{12}O_2Cl_2S$ requires C, 32·9; H, 5·5; Cl, 32·4%). It is appreciably soluble in water and readily soluble in most organic solvents with the exception of light petroleum. In view of the unexpected nature of this product the analyses were repeated—with similar results. The substance was also produced when the chloro-sulphide was (i) dropped into a mixture of fuming (2 vols.) and concentrated (1 vol.) nitric acid cooled in a freezing mixture; (ii) dissolved (0·94 g.) in glacial acetic acid (2 c.c.), mixed with hydrogen peroxide (0·7 g. in 2 c.c. of 60% acetic acid) slowly with cooling, and kept at laboratory temperature for 48 hours; and (iii) heated for 2 hours in boiling glacial acetic acid with chromic anhydride (twice the calculated amount to produce a sulphone).

$\gamma\gamma'$-Diphenoxydipropyl Sulphide $(PhO\cdot C_3H_6)_2S$.—The chloro-sulphide (1·2 g.) was heated at 180° for 2 hours with phenol (6 g.) and sodium ethoxide (from 0·3 g. of sodium). The mixture was made acid and distilled with steam. The residual oil solidified when washed with a little aqueous alkali, and was then recrystallised from methyl alcohol; m. p. 45° (Found: C, 71·35; H, 7·4. $C_{18}H_{22}O_2S$ requires C, 71·35; H, 7·3%).

$\gamma\gamma'$-Di-p-tolyloxydipropyl sulphide, prepared in a similar way from *p*-cresol, had m. p. 50—52° (Found: C, 72·9; H, 7·9. $C_{20}H_{26}O_2S$ requires C, 72·7; H, 7·9%).

Action of Piperidine on the Chloro-sulphide.—When a mixture of the chloro-sulphide with piperidine (8 mols.) was kept for 24 hours, crystals of piperidine hydrochloride separated out. The mixture was made alkaline and distilled with steam. The residual oil

was removed in ether, the extract dried and evaporated, when *$\gamma\gamma'$-dipiperidinodipropyl sulphide*, $(C_5H_{10}N\cdot C_3H_6)_2S$, was left as an oil which did not crystallise. It readily yielded a *picrate*, which crystallised from methyl alcohol in yellow needles, m. p. 199—200° (Found: C, 45·3; H, 5·8. $C_{28}H_{38}O_{14}N_8S$ requires C, 45·3; H, 5·2%).

Action of Potassium Cyanide.—The chloro-sulphide (1·87 g.) was heated in boiling ethyl alcohol for 9 hours with potassium cyanide (2 g. = 3 mols.). The alcohol was evaporated, water added, the precipitated oil removed in ether, and the ether evaporated. The crude dinitrile thus obtained was at once hydrolysed by boiling with concentrated hydrochloric acid (15 c.c.) for 2 hours. The cold diluted solution was extracted several times with ether, and the extract on evaporation left a solid (0·8 g.) which was crystallised once from a little water and once from benzene–light petroleum. This substance was thiodibutyric acid, of m. p. 99—101° (Gabriel, *loc. cit.*, and Davies, J., 1920, **117**, 297) (Found: by titration, equiv., 105. Calc., 103·1).

Action of Potassium Sulphide.—The chloro-sulphide (4·0 g.) was heated for 3 hours with a boiling ethyl-alcoholic solution of freshly prepared potassium sulphide (from 4·8 g. of potassium hydroxide); the mixture was then distilled with steam. The residual oil, which solidified on cooling, crystallised from carbon disulphide–light petroleum as a white powder melting indefinitely between 50° and 70°. Repeated crystallisation failed to separate any substance of sharp melting point. This material, although evidently not a pure chemical individual, had approximately the composition of a polymeride of *hexamethylene disulphide* (Found: C, 48·0; H, 8·4; *M*, cryoscopic in camphor, 1400, 1740. $C_6H_{12}S_2$ requires C, 48·65; H, 8·1%; *M*, 148). It closely resembles the "polymeric" diethylene disulphide which results from the action of alkali sulphides upon ethylene dibromide or dichlorodiethyl sulphide, and both are probably mixtures of substances having a long open-chain structure (compare Bennett and Whincop, J., 1921, **119**, 1861; Staudinger, *Helv. Chim. Acta*, 1925, **8**, 67).

Comparison with $\beta\beta'$-Dichlorodiethyl Sulphide with respect to Speed of Reaction with Alcoholic Sodium Hydroxide.—A solution of dichlorodiethyl sulphide in ethyl alcohol (10 c.c.; 0·23 mol. per litre) was added to boiling alcoholic sodium hydroxide (25 c.c.; 0·5115*N*), and the mixture boiled under reflux. It was found by titration that after 5 minutes the reaction had completed itself to the extent of 71·5%. An approximately equivalent solution of $\gamma\gamma'$-dichlorodipropyl sulphide (10 c.c.; 0·25 mol. per litre) was mixed with the same volume of the same solution and boiled for 5 hours; the reaction had then completed itself to the extent of 71·7%.

We wish to express our thanks to the West Riding County Council for a scholarship which has enabled one of us (A. L. H.) to take part in this investigation, and to the Chemical Society for a grant which has defrayed much of the expense involved.

THE UNIVERSITY, SHEFFIELD. [*Received, September 1st*, 1925.]

CCCLXVI.—*Researches on Sulphuryl Chloride. Part IV. Further Studies on a New Chlorinating Agent. Preparation of Polychloro-derivatives of Toluene.*

By OSWALD SILBERRAD.

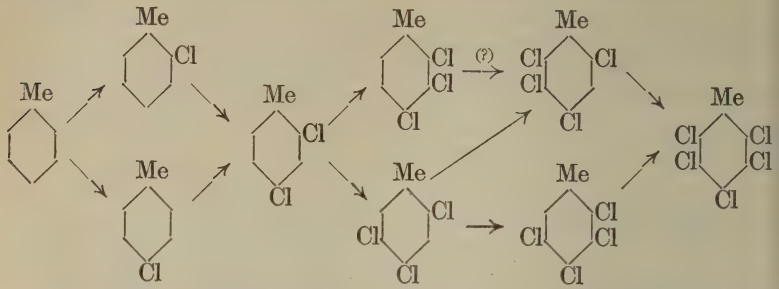
IN previous communications (J., 1921, **119**, 2029; 1922, **121**, 1015) it was shown that anhydrous aluminium chloride and sulphuryl chloride interact to form aluminium chlorosulphoxide, $AlCl_3{:}SO_2$; and that in the presence of sulphur, aluminium sulphur chloride, $AlCl_3{:}SCl{\cdot}SCl{:}AlCl_3$, is produced: further, that towards sulphuryl chloride both these compounds act as potent catalysts, the latter being quite the most convenient chlorinating agent at our disposal, and also one of the most powerful.

It is with the object of extending our knowledge of this reagent, hitherto restricted to its action on benzene (*loc. cit.*), that the present research on the chlorination of toluene was undertaken.

The only earlier work that has any bearing on this subject is that of Witte (*Pharm. Rec.*, New York, Dec. 16, 1889), Tohl and Eberhard (*Ber.*, 1893, **26**, 2943), and Böeseken (*Rec. trav. chim.*, 1911, **30**, 381). These experimenters all investigated the action of sulphuryl chloride on toluene in the presence of aluminium chloride under conditions conducive to the Friedel-Crafts reaction and obtained mixtures composed of *o*- and *p*-toluenesulphonyl chlorides as the chief ingredients, together with lesser amounts of *o*- and *p*-chlorotoluenes, ditolylsulphone (T. & E.), and *o*- and *p*-toluenesulphonic acids (B.).

If, however, sulphuryl chloride containing about 1% of sulphur chloride be run into a mixture of toluene and anhydrous aluminium chloride previously heated at about 70°, aluminium sulphur chloride is instantaneously formed and chlorination takes place as rapidly as the mixture is added, an almost theoretical yield of mono-, di-, tri-, or penta-chlorotoluene being produced with equal ease and rapidity by simply adjusting the relative proportions of hydrocarbon and reagent. Progressive chlorination proceeds in accord-

ance with the following scheme, indeed the isomerides therein depicted are produced almost to the exclusion of all others :



The nature and proportions of the various isomerides produced differ sufficiently from those hitherto obtained by direct chlorination to render it necessary to refer briefly to each stage of the chlorination.

Monochlorotoluenes.—The ratio of the para-compound to the ortho in the product is slightly higher than that in the case of chlorination in presence of an aluminium–mercury couple (Cohen and Dakin, J., 1891, **79**, 1119) but lower than that obtained by the electrolysis of a mixture of toluene and hydrochloric acid (Cohen, Dawson, and Crossland, J., 1905, **87**, 1035).

Dichlorotoluene.—Here the 2 : 4-isomeride is produced almost in a state of chemical purity. This is surprising, for the only chlorotoluene higher than the mono-derivative hitherto produced by the action of sulphuryl chloride on toluene is the 3 : 4-isomeride, which Tohl and Eberhardt obtained in small quantity by heating a mixture of these substances in a sealed tube at 160° (*Ber.*, 1893, **26**, 2942). All other means of preparing dichlorotoluene by direct chlorination of the hydrocarbon give rise to complex mixtures of the following isomerides—3 : 4- (Beilstein and Kuhlberg, *Annalen*, 1868, **146**, 319), 2 : 6- (Aronheim and Dietrich, *Ber.*, 1875, **8**, 1402), 2 : 4- and 2 : 3- (Seelig, *Annalen*, 1887, **237**, 157), 2 : 5- (Wynne, P., 1901, **17**, 116); compare also Cohen and Dakin (J., 1901, **79**, 1119), who, by working with *o*- and *p*-chlorotoluene separately, showed that the product obtained by chlorinating toluene in the presence of an aluminium–mercury couple contained all these isomerides with the possible exception of 2 : 5-dichlorotoluene.

Trichlorotoluenes.—As was to be expected from the nature of the dichlorination product, the addition of the required quantity of the new reagent to toluene leads to the formation of practically nothing but the 2 : 4 : 5- and 2 : 3 : 4-trichloro-derivatives, indeed they are so free from other isomerides that these two compounds can be easily separated, and in this respect the product compares very favourably with that obtained by any of the known processes

of chlorinating toluene, which lead to mixtures of 2 : 3 : 4-, 2 : 4 : 6-, 2 : 3 : 6-, and 2 : 4 : 5-trichlorotoluenes (Limpricht, *Annalen*, 1866, **139**, 303; Beilstein and Kuhlberg, Aronheim and Dietrich, Seelig, *loc. cit.*, Cohen and Dakin, J., 1902, **81**, 1324).

Tetrachlorotoluenes.—In this instance some doubt appears to exist as to precisely what isomerides are formed by direct chlorination. Limpricht (*loc. cit.*, p. 327) obtained a tetrachlorotoluene melting at 96° (the 2 : 3 : 4 : 5-isomeride melts at 98·1°). On the other hand, working with antimony pentachloride, Beilstein and Kuhlberg (*Annalen*, 1869, **150**, 287) isolated a compound the m. p. of which (91—92°) agreed more closely with that of the 2 : 3 : 4 : 6-isomeride (91·5—92°). Again, Cohen and Dakin (J., 1904, **85**, 1283), who subsequently investigated this subject by further chlorinating the trichloro-compounds in presence of an aluminium–mercury couple, obtained from the 2 : 3 : 4-isomeride a product, melting at 89—91° and giving a nitro-derivative, m. p. 149°, which they concluded to be 2 : 3 : 4 : 6-tetrachlorotoluene (m. p. 91·5—92°; nitro-derivative, m. p. 153°); and from 2 : 4 : 5-trichlorotoluene, a product melting at 86—88° which they took to be the 2 : 3 : 4 : 5-derivative. The same experimenters, however, subsequently showed that this particular isomeride melts at 97—98° (J., 1906, **89**, 1453), so there still remains some doubt as to its formation. The results obtained with the new chlorinating agent appear to confirm this and Limpricht's observation that the isomeride (the 2 : 3 : 4 : 5-) is the principal one obtained by introducing four chlorine atoms into toluene. The method cannot, however, be recommended for the preparation of any of the tetrachlorotoluenes, for not only are the isomerides formed in such proportions that there is considerable difficulty in separating them, but also the trichlorotoluenes show a great tendency to pass directly to the pentachloro-derivative under the influence of the reagent, behaving in this respect in a manner analogous to that observed in the preparation of pentachlorobenzene (Silberrad, J., 1922, **121**, 1020). In this connexion it is to be observed that both these compounds are penta-substituted derivatives of benzene.

Pentachlorotoluene.—Unlike other powerful chlorinating agents, which lead to products contaminated with hexachlorobenzene (Beilstein and Kuhlberg, *Annalen*, 1869, **150**, 898; Fichter and Glantzstein, *Ber.*, 1916, **49**, 2473), the new reagent does not attack the side chain at all; this is neither substituted nor split off. Pentachlorotoluene, which is formed with the utmost ease, is the end-product of the reaction; the yield is nearly theoretical and the product practically pure.

Experimental.

The preparation of the reagent and the general procedure adopted were similar to those previously described (J., 1922, **121**, 1018). The apparatus consisted of a suitable-sized flask fitted with and ground to a 6-bulb reflux condenser,* the upper portion of which was connected through a trap to a flask containing 10 litres of water to absorb the sulphur dioxide and hydrogen chloride which are copiously evolved during the reaction. The required quantity of the reagent (*i.e.*, sulphuryl chloride containing 1% of sulphur chloride) was run into toluene mixed with anhydrous aluminium chloride, the apparatus being immersed in a water-bath previously heated to about 70°. Chlorination took place at the rate at which the reagent was run in. The actual time occupied was approximately ½ hour per chlorine atom introduced; thus, trichlorotoluene was obtained after 1½ hours, and the pentachloro-derivative after 2½ hours. This period may be much shortened if desired.

2- *and* 4-*Chlorotoluenes.*—On adding the chlorinating agent (280 g. = 2½% excess) to a mixture of toluene (184 g.) and anhydrous aluminium chloride (10 g.) under the conditions described above, a vigorous reaction took place at once; the product was at first brilliant purple, but rapidly became ruddy-brown. After washing with hot water, 247 g. of an oil were obtained which distilled almost wholly between 153—165°/758 mm., yielding 222 g. in one instance and 227 g. in another (88% of the theoretical). The nature and proportions of the isomerides present were determined by oxidising 50 g. of the product with permanganate; 21 g. of *p*- (m. p. 236°) and 16 g. of *o*-chlorobenzoic acid (m. p. 137°) were obtained; no meta-acid could be detected.

2 : 4-*Dichlorotoluene.*—The chlorinating agent (560 g.) was run into a mixture of toluene (184 g.) and anhydrous aluminium chloride (10 g.) as above described, and the reaction completed by heating at 100° for a few minutes, the total time occupied being 1 hour. The deep brown reaction product yielded 240 g. of a heavy oil when boiled with water, and 220 g. of almost pure 2 : 4-dichlorotoluene on subsequent fractionation.

Preparation of 2 : 4-*dichloro*-3 : 5-*dinitrotoluene.* In order to identify it, the above oil (100 g.) was run into a mixture of nitric acid (200 c.c.; *d* 1·48) and sulphuric acid (400 c.c.; *d* 1·84) at 60°; the reaction mixture was then heated at 105° for ½ hour. On pouring the product into water, an oil separated which, on cooling, set to a pale yellow, crystalline mass: this, filtered off from the

* A very convenient form of apparatus for the purpose is obtainable from Messrs. Townson and Mercer, Ltd., 34 Camomile St., E.C.

adherent oil, washed with cold alcohol, and recrystallised from the same solvent, yielded 94 g. of pure 2 : 4-dichloro-3 : 5-dinitrotoluene, m. p. 104·3° (corr.) (Cohen and Dakin give 104°, and Seelig 102°) (Found : Cl, 28·3%).

Preparation of 2 : 4-*dichloro*-3 : 5-*dinitrobenzoic acid.* The oily residue from which the above product had separated was boiled (20 g.) with nitric acid (200 c.c.; *d* 1·42) and mercuric nitrate (2 g.) for 120 hours. On cooling, 11 g. of 2 : 4-dichloro-3 : 5-dinitrobenzoic acid (m. p. 210—211°. Found : Cl, 25·22%) crystallised; no other isomeride could be detected.

It must therefore be concluded that on chlorinating toluene as above described the product consists of almost pure 2 : 4-dichlorotoluene.

2 : 4 : 5- *and* 2 : 3 : 4-*Trichlorotoluenes.*—Into a mixture of toluene (184 g.) and anhydrous aluminium chloride (10 g.) at 70°, the chlorinating agent (840 g.) was run during 1½ hours. On boiling the dark vandyke-brown reaction mass with water, and fractionating, the oily product (324 g.) passed over between 215° and 245°; this slowly set to a crystalline mass consisting of almost equal parts of 2 : 4 : 5- and 2 : 3 : 4-trichlorotoluenes (yield 83%).

Isolation and identification of 2 : 4 : 5-*trichlorotoluene.* The crystalline mass was freed from oil, washed with cold alcohol, and recrystallised from the same solvent, whereby 151 g. of pure 2 : 4 : 5-trichlorotoluene separated as glistening needles or leaflets, m. p. 82·4° (corr.) (Found : Cl, 54·3%). From this, 2 : 4 : 5-trichloro-3 : 6-dinitrotoluene, m. p. 227°, was prepared.

Isolation and identification of 2 : 3 : 4-*trichlorotoluene.* The residual oil and mother-liquors from which the 2 : 4 : 5-isomeride had been separated yielded, on fractionation, 158 g. of an oil, b. p. 225—239°, together with 17 g. of a lower fraction which consisted chiefly of dichlorotoluene. On standing, the main fraction set to a wax-like mass; this was mascerated with 300 c.c. of cold alcohol. The residue, 7·2 g., consisted chiefly of the 2 : 4 : 5-isomeride and melted after several recrystallisations at 81—82°. Water was added to the alcoholic extract until a permanent opalescence appeared, just sufficient alcohol added to redissolve this at 20°, and the solution kept at 0° for several days; the wax-like, crystalline solid which was obtained (74 g.), on recrystallisation from alcohol, melted at 41° and proved to be 2 : 3 : 4-trichlorotoluene (Found : Cl, 54·4%). The yield of the pure substance was 56 g.

Preparation of 2 : 3 : 4-*trichloro*-5 : 6-*dinitrotoluene.* On adding water to the mother-liquors from which 2 : 3 : 4-trichlorotoluene had crystallised an oil (70 g.) was precipitated which, on nitration as described in the preparation of 2 : 4-dichloro-3 : 5-dinitrotoluene,

yielded 64 g. of 2 : 3 : 4-trichloro-5 : 6-dinitrotoluene, m. p. 141° (Found : Cl, 44·2%). No derivatives of other isomerides could be isolated. The above results therefore correspond to a yield of 40% of 2 : 4 : 5-trichlorotoluene and 34% of the 2 : 3 : 4-isomeride.

2 : 3 : 4 : 5-*Tetrachlorotoluene*.—The direct preparation of this compound from toluene is not to be recommended, because on treating toluene (184 g.) with sufficient of the chlorinating agent (1120 g.) to produce the tetrachloro-derivative as above described, besides trichlorotoluene (104 g.) and pentachlorotoluene (130 g.), a mixture of isomeric tetrachlorotoluenes (87 g.) is obtained, the separation of which presents the greatest difficulty. The trichlorotoluene so produced consists chiefly of the 2 : 3 : 4-isomeride, from which it would appear that when a mixture of 2 : 3 : 4- and 2 : 4 : 5-trichlorotoluenes is subjected to the action of the new chlorinating agent the 2 : 4 : 5-isomeride is converted into the pentachloro-derivative before the 2 : 3 : 4-compound is attacked to any appreciable extent. An experiment with a mixture of these isomerides confirmed this conjecture, whilst a further experiment with pure 2 : 3 : 4-trichlorotoluene led to a result similar to that above described where toluene was the initial material. Pure 2 : 4 : 5-trichlorotoluene was therefore used for the preparation of the tetrachloro-derivative : to this end, this compound (98 g.) was mixed with anhydrous aluminium chloride (5 g.), the surrounding water-bath raised to incipient ebullition until the trichloro-compound had completely melted, and the chlorinating agent (70 g.) was then run in. On cooling, the product set to a dark brown, scaly mass. This was boiled with 100 c.c. of toluene and 50 c.c. of water, the toluene solution separated, and mixed with an equal volume of alcohol; the bulk of the pentachlorotoluene present (12 g.) slowly crystallised in long, glistening needles.

The mother-liquor, which contained the whole of the tetrachlorotoluene, was freed from solvent and fractionally distilled. The first fraction, b. p. 230° ± 15° (11 g.), consisted chiefly of unaltered 2 : 4 : 5-trichlorotoluene.

The second fraction, b. p. 273° ± 15° (49 g.), was again treated as above described for the removal of pentachlorotoluene, and a further 2 g. were thus removed; the mixed solvent was then distilled off and the residue ground up with 25 c.c. of cold absolute alcohol; this treatment, repeated twice, the alcoholic extract being filtered off each time, yielded 4 g. of 2 : 4 : 5-trichlorotoluene. The solid residue (40 g.) consisted chiefly of 2 : 3 : 4 : 5-tetrachlorotoluene, and after eleven recrystallisations from a series of solvents (light petroleum–benzene; alcohol; and dilute alcohol) was obtained in long, flexible, silky needles, closely resembling asbestos

in appearance, melting at 98·1° (corr.) and giving 2 : 3 : 4 : 5-tetrachloro-6-nitrotoluene, m. p. 159·6° (corr.), on nitration under conditions similar to those described above in the preparation of 2 : 4-dichloro-3 : 5-dinitrotoluene.

Identification of 2 : 3 : 4 : 6-*tetrachlorotoluene and preparation of* 2 : 3 : 4 : 6-*tetrachloro-5-nitrotoluene.* The compounds present in the mother-liquors from which the 2 : 3 : 4 : 5-isomeride had separated were bulked, freed from solvent, redissolved in alcohol, and roughly separated into three fractions by precipitation. Each fraction was nitrated as described above, and the nitro-products were fractionally crystallised from alcohol of varying degrees of dilution. Worked up in this manner, the first and second fractions only yielded products having constant melting points; that from the former melted at 159° and was evidently 2 : 3 : 4 : 5-tetrachloro-6-nitrotoluene, and that from the latter melted at 154° and appeared to be 2 : 4 : 5 : 6-tetrachloro-3-nitrotoluene (Found: Cl, 51·1. $C_7H_3O_2NCl_4$ requires Cl, 51·6%). It seems probable, therefore, that the compound, m. p. 153°, obtained by Cohen and Dakin as the final product of nitrating 2 : 3 : 4 : 6-tetrachlorotoluene (J., 1904, **85**, 1231) was the true nitro-derivative and that the substance melting at 131—134° which they took to be 2 : 3 : 4 : 5-tetrachloro-3-nitrotoluene owed its low melting point to the presence of the unnitrated compound; indeed, as these investigators point out, their analysis shows the presence of a considerable quantity (about 10%) of this impurity. The true melting point of 2 : 4 : 5 : 6-tetrachloro-3-nitrotoluene therefore appears to be 154°. Unfortunately, the quantity obtained by this most tedious process was too small to admit of a more complete identification.

Pentachlorotoluene.—Toluene (184 g.) mixed with aluminium chloride (10 g.) was treated with the chlorinating agent (1632 g. = 20% excess) as above described, the reaction being completed by heating in the boiling water-bath for ½ hour. During the chlorination the reacting mixture became successively a brilliant purple liquid, a red-brown liquid, a dark brown, scaly mass, an almost white, crystalline lump. On boiling the product with 3 litres of benzene and 100 c.c. of water, separating the benzene solution, and allowing it to cool, the pentachloro-compound (380 g.) crystallised in almost colourless needles which, on recrystallisation, melted at 217·5° (uncorr.) (Found: Cl, 67·1%). Pentachlorotoluene is soluble in 3·4 vols. of toluene at 87° and in 22 vols. at 17°.

Action of the Chlorinating Agent on Pentachlorotoluene.—A mixture of pentachlorotoluene (100 g.), anhydrous aluminium chloride (10 g.), and the chlorinating agent (200 g.) was heated on the water-bath for 8 hours. On recrystallising the product from benzene,

88 g. of pentachlorotoluene, m. p. 217°, were recovered, whilst the residue, which was almost insoluble in benzene, after recrystallisation from chlorobenzene, melted at 272—274° and appeared to be a condensation product, possibly nonochlorophenyltolylmethane, $C_6Cl_5 \cdot CH_2 \cdot C_6Cl_4 \cdot CH_3$, produced by the condensation of pentachlorotoluene (2 mols.) under the influence of anhydrous aluminium chloride (Found: Cl, 64·4. $C_{14}H_5Cl_9$ requires Cl, 65·0%).

Pentachlorobenzoic acid.—Owing to the great similarity existing between hexachlorobenzene and pentachlorotoluene, and the very slight influence the addition of the former has on the melting point of the latter, the purity of the pentachlorotoluene recovered as above described was further established by oxidising 20 g. with nitric acid (200 c.c.; *d* 1·42) and mercury (2 g.), by boiling the mixture until solution was complete (150 hours). On pouring the acid liquor into water, a white, crystalline precipitate separated; this redissolved completely in ammonia and proved to be practically pure pentachlorobenzoic acid, m. p. 199·5° (Found: Cl, 59·6. Calc., Cl, 60·2%). The acid is very soluble in toluene or alcohol. It has the extraordinary property of separating from the latter solution as an oil on dilution, in spite of its high melting point. It is best crystallised from toluene–light petroleum, from which it separates in large, truncated prisms.

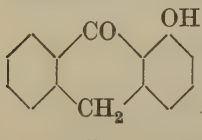
My thanks are due to Messrs. A. Boake Roberts and Co. Ltd., of Stratford, for supplying the sulphuryl chloride required for this investigation.

THE SILBERRAD RESEARCH LABORATORIES,
BUCKHURST HILL, ESSEX. [*Received, September 11th,* 1925.]

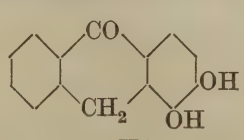
CCCLXVII.—*Reduction Products of the Hydroxyanthraquinones. Part VII.*

By WILLIAM BERTRAM MILLER and ARTHUR GEORGE PERKIN.

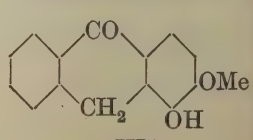
A COMPARISON of the formulæ of the hydroxyanthrones obtained during the reduction of 1-hydroxyanthraquinone and of 1 : 2-dihydroxyanthraquinone (alizarin) is of interest because, whereas the former (I) contains the hydroxyl adjacent to the carbonyl group, in the latter (II) the hydroxyls are in the 3 : 4-positions thereto.



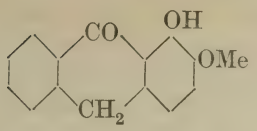
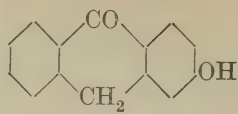
(I.)



(II.)



(III.)

(IV.)   (V.)

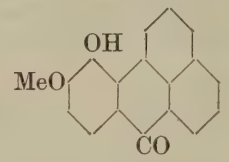
As is well known, the hydroyxl group adjacent to the carbonyl group in hydroxy-ketones differs in properties from those present in other positions, and to explain this, it is assumed to be involved with the carbonyl to form an ortho-quinonoid, or a six-membered, chelate grouping (Sidgwick and Callow, J., 1924, **125**, 527), or that in any case some form of attraction exists between the two. If the reduction of the hydroxyanthraquinones follows the scheme applicable to anthraquinone itself,

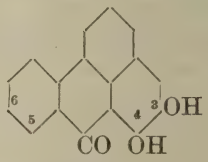


it is reasonable to assume that owing to the attraction of the α-hydroxyl for carbonyl, in the change from *b* to *c*, these will take up adjacent positions, as, indeed, occurs with the 1-hydroxyanthrone (I) derived from 1-hydroxyanthraquinone. For a similar reason, it is to be expected that, as the α-hydroxyl is present in alizarin also, this on reduction will yield the 1 : 2-dihydroxyanthrone, whereas as a matter of fact the 3 : 4-dihydroxy-compound is produced (II). To account for this, it seems likely that in this case the attraction of the α-hydroxyl for the carbonyl is either non-existent, or is suppressed by the greater attraction of the β-hydroxyl for the para-position thereto, and thus in the change from (*b*) to (*c*) the 3 : 4-dihydroxy-compound results. In support of this is the fact that 2-hydroxyanthraquinone when reduced gives 3-hydroxyanthrone (V), and therefore there is reason to presume that in these cases the β-hydroxyl is the determining factor, or that, in other words, a para-quinonoid structure is preferred even when α- and β-hydroxyls are simultaneously present. It was interesting, therefore, to study the behaviour of alizarin 2-methyl ether * in these circumstances, for owing to the etherification of the 2-hydroxyl group this compound more closely resembles in general properties 1-hydroxyanthraquinone than alizarin itself and it was to be anticipated that 1-hydroxy-2-methoxyanthrone (IV) would result. With stannous chloride and hydrochloric acid as reducing agent, this is the case, although in

* According to Graebe and Thode (*Annalen*, 1906, **349**, 207), alizarin dimethyl ether reduced with zinc dust and ammonia gives 3 : 4-dimethoxyanthrone, together with a second compound, probably 1 : 2-dimethoxyanthracene.

addition to this compound, which is the main product, a small amount of 4-hydroxy-3-methoxyanthrone (deoxyalizarin monomethyl ether; III) is produced, accompanied by much viscid matter. In order to determine the constitution of these compounds, recourse was had to the benzanthrone reaction, followed by a study of the behaviour of each product when methylated, by means of methyl iodide and alkali. From the pale yellow anthrone (III) in this manner, benzalizarin methyl ether (VI) was obtained, and in proof of this an identical compound was prepared from benzalizarin itself (J., 1920, **117**, 702).

(VI.) 



(VII.)

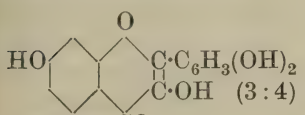
On the other hand, the orange-coloured anthrone (IV) gave, although in small amount, a compound to which formula (VII) has been assigned, demethylation having occurred during the reaction; it has not been ascertained, however, whether the hydroxyls occupy the 3 : 4- or 5 : 6-positions. Whereas it was previously shown (*loc. cit.*) that both hydroxyls of benzalizarin are readily methylated with methyl iodide and alkali, with the compound (VII), for which the name iso*benzalizarin* is suggested, this is not the case, as under drastic treatment with these reagents only a monomethyl ether is produced. Evidently, therefore, a hydroxyl is here present adjacent to the carbonyl group, and this view is supported by the fact that, whereas *monoacetyl*iso*benzalizarin* is readily obtained, the *diacetyl* compound can be prepared therefrom only by prolonged digestion with boiling acetic anhydride and pyridine.

Benzalizarin and *iso*benzalizarin differ widely in their dyeing properties with mordants, for whereas the former gives shades analogous to those of alizarin itself (*loc. cit.*), the latter dyes yellow and is scarcely a strong colouring matter. This is of interest, because it is generally assumed that the tinctorial properties of the hydroxyanthraquinone dyestuffs, as, *e.g.*, alizarin, are due at least in part to an ortho-quinonoid or some similar arrangement in which the 1-hydroxy- and the adjacent carbonyl group are involved. In such a sense, however, benzalizarin must be regarded as a para-quinonoid, and *iso*benzalizarin as an ortho-quinonoid dyestuff, and this suggests that the dyeing properties of alizarin,* which resemble those of benzalizarin but differ markedly from those of *iso*benzalizarin,

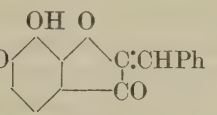
* A para-quinonoid structure was suggested by one of us for the mono-alkali salts of the hydroxyanthraquinones (J., 1899, **75**, 433).

may be due to the presence of a para-quinonoid rather than to an ortho-quinonoid grouping.

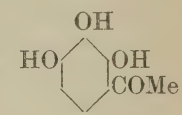
If a survey be made of the phenolic mordant dyestuffs, and more especially of those in which adjacent hydroxyl groups are present, it will be observed that for most of them a para-quinonoid arrangement only is possible; of the very numerous instances which can be given, fisetin (VIII) and the dihydroxybenzylidenecoumaranone (IX; Friedländer and Rudt, *Ber.*, 1896, **29**, 878), both powerful dyestuffs, may be cited.



(VIII.)



(IX.)



(X.)

On the other hand, whereas other colouring matters of this adjective class, as, for instance, gallacetophenone (X) and the hydroxyanthraquinones, may be considered to dye by virtue of either an ortho- or para-quinonoid grouping, there is, with the exception of such feeble dyes as euxanthone, which do not contain adjacent hydroxyls, an almost complete lack of colouring matters to which an ortho-quinonoid grouping only can be applied.

Experiments are in progress with the hope of obtaining, in addition to *iso*benzalizarin, dyes which come under the latter category.

A preliminary study of the behaviour of anthrapurpurin 2 : 7-dimethyl ether on reduction has at present resulted in the isolation, in small yield, of but one anthrone, which is probably the 4-hydroxy-3 : 6-dimethoxy-compound. Much viscid matter is simultaneously produced.

Experimental.

Alizarin 2-Methyl Ether.—To a boiling solution of commercial alizarin paste (150 g.) in 10% sodium hydroxide solution (525 c.c.), methyl sulphate (110 c.c.) was gradually added, and the mixture was repeatedly treated with sodium hydroxide solution (50 c.c.) and the equivalent quantity of methyl sulphate.* The product was collected, stirred with sodium carbonate solution to remove alizarin, the crude methyl ether (30 g.) dissolved in benzene and precipitated therefrom as potassium salt by alcoholic potassium hydroxide; some alizarin dimethyl ether remained in solution. The potassium salt was decomposed with acid, and the alizarin 2-methyl ether thus obtained was recrystallised from benzene until the melting point, 229–230°, was constant (Found: C, 70·8; H, 4·05%). In addition to the alizarin dimethyl ether, m. p. 214–215°, a second

* A modification of the method of Graebe and Thode (*loc. cit.*). In all, 875 c.c. of caustic soda solution and 195 c.c. of methyl sulphate were employed.

dimethyl ether of identical appearance but melting at 169–171° could be isolated from the final mother-liquor if the crude alizarin 2-methyl ether was crystallised from benzene. This was evidently a methylalizarin dimethyl ether derived from 2-methylalizarin present in the dyestuff employed, in that it could not be produced by the further methylation either of alizarin 2-methyl ether or of alizarin dimethyl ether with methyl sulphate and alkali.

Reduction. A mixture of alizarin 2-methyl ether (10 g.), stannous chloride (100 g.), and 33% hydrochloric acid (500 c.c.) was boiled for 1¼ hours. The crystals, without apparent solution, were converted into a brown tar which, on cooling, solidified to a hard, brittle mass, some yellow crystals simultaneously separating from the acid liquid. The ground product was dissolved in about 100 c.c. of alcohol, and the crystals which separated on cooling were collected (yield 6 g.). The dark-coloured mother-liquor on evaporation yielded an orange-brown resin, from which nothing definite could be isolated. The crystals when extracted with a little boiling benzene gave a pale yellow residue (A) in small amount, whereas from the extract orange-red needles (B) separated on cooling.

(A), crystallised from much benzene with the aid of animal charcoal, gave pale yellow needles, which were recrystallised from alcohol (Found: C, 75·1; H, 5·1; CH_3, 6·1. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0; CH_3, 6·25%). 4-*Hydroxy*-3-*methoxyanthrone*, m. p. 202°, yields an *acetyl* compound, which crystallises in lemon-yellow needles, m. p. 185—186°, and is oxidised by chromic acid in acetic acid solution to acetylalizarin 2-methyl ether.

(B) crystallised from alcohol, in which it was less soluble than A, in orange-red needles, m. p. 135—137° (Found: C, 74·9; H, 5·0; CH_3, 6·2. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0; CH_3, 6·25%). 1-*Hydroxy*-2-*methoxyanthrone* is thus obtained in much larger amount than its isomeride. Like this, on oxidation it yields alizarin 2-methyl ether. The *diacetyl* derivative crystallises from alcohol–acetic acid in yellow plates, m. p. 202° (Found: C, 70·3; H, 4·9; $C_2H_4O_2$, 36·7. $C_{19}H_{16}O_5$ requires C, 70·4; H, 4·9; $C_2H_4O_2$, 37·0%).

Benzalizarin Monomethyl Ether.—A mixture of 4-hydroxy-3-methoxyanthrone (4 g.), sulphuric acid (47 c.c.), water (23 c.c.), and glycerol (8 g.) was gradually heated at 125—130°, being well stirred, and kept for 1 hour. The solution when cold was poured into water, the green precipitate collected, washed, dried, and in the ground condition repeatedly treated with boiling alcohol. The extract was concentrated, poured into much ether, the solution filtered, washed with water, evaporated to dryness, and the pale brown, friable residue (1·4 g.) titurated with ether to remove resinous matter. By acetylation, crystals were obtained which, after re-

crystallisation from alcohol–acetic acid, gave 0·4 g. of pale yellow needles, m. p. 205—207° (Found : C, 75·3; H, 4·15; CH_3, 4·85. $C_{20}H_{14}O_4$ requires C, 75·4; H, 4·4; CH_3, 4·7%).

This compound, which is *acetylbenzalizarin methyl ether*, when hydrolysed with hydrochloric acid in presence of acetic acid gave 86·13% of *benzalizarin monomethyl ether*, whereas theory requires 86·8%. The latter is thus obtained as long, orange needles, m. p. 247—249°, sparingly soluble in caustic soda solution and in alcohol, soluble in sulphuric acid with a violet-red coloration (Found : C, 78·0; H, 4·55. $C_{18}H_{12}O_3$ requires C, 78·3; H, 4·3%).

Sulphuric acid, in presence of acetic acid, gives the oxonium sulphate, as long, hair-like, maroon-coloured needles.

The product from the Zeisel determination of the acetyl compound was poured into bisulphite solution. The crystals produced had all the properties of benzalizarin and yielded an acetyl compound, the melting point of which, 202—204°, was slightly higher than that previously given (*loc. cit.*).

Benzalizarin monomethyl ether was also obtained by the partial methylation of benzalizarin itself. Acetylbenzalizarin (0·95 g.) in boiling methyl alcohol (20 c.c.) and methyl iodide (8 c.c.) was gradually treated with caustic potash (0·35 g.) in methyl alcohol. The crystalline substance produced (0·64 g.), m. p. 247—249° after recrystallisation, was identical with the benzalizarin methyl ether described above. A small amount of benzalizarin dimethyl ether was present in the original mother-liquor.

iso*Benzalizarin*.—A mixture of 1-hydroxy-2-methoxyanthrone (substance B) (4 g.), sulphuric acid (47 c.c.), water (2·5 c.c.), and glycerol was heated at 120—130° for 1 hour. The solution was poured into water, the precipitate collected, dried, and the colouring matter present isolated by means of the alcohol and ether treatment described under benzalizarin methyl ether. The orange-red powder thus obtained (1·4 g.) was washed with acetone to remove resin, and after recrystallisation from the same solvent gave 0·6 g. of orange-yellow needles. These by treatment with boiling acetic anhydride and pyridine for a few seconds gave a crystalline deposit of the *acetyl* compound, which crystallised from much acetone in bright orange-yellow, flat needles (0·3 g.); * m. p. 243—245° (Found : C, 74·85; H, 4·35. $C_{19}H_{12}O_4$ requires C, 75·0; H, 3·9%).

This compound, *monoacetyl*iso*benzalizarin*, is very sparingly soluble in acetone or alcohol. It contains no methoxy-group and

* This small yield of *iso*benzalizarin was evidently due to the 1-hydroxy-2-methoxyanthrone suffering alteration on heating with sulphuric acid. An amorphous product was thus produced which was soluble in caustic soda with a reddish-brown tint, and in cold acetone with a red colour.

when hydrolysed gives 86·6% of iso*benzalizarin*, theory requiring 86·2%. This crystallised from nitrobenzene in orange needles, m. p. 260—262° (Found : C, 77·8; H, 3·9. $C_{17}H_{10}O_3$ requires C, 77·9; H, 3·8%).

*iso*Benzalizarin gives with sulphuric acid a green, fluorescent, orange-red liquid and with boiling dilute alkalis, orange-yellow solutions with which baryta water yields orange-red precipitates. By digesting the monoacetyl derivative with boiling alcoholic potassium acetate, orange needles of a potassium salt are deposited. It is unaltered by long boiling with hydriodic acid. *iso*Benzalizarin is somewhat resistant to full acetylation, but by a long digestion with acetic anhydride and pyridine a *diacetyl* derivative is obtained which crystallises from acetic anhydride in yellow needles, m. p. 214° (Found : C, 73·3; H, 4·0. $C_{21}H_{14}O_5$ requires C, 72·8; H, 4·0%).

iso*Benzalizarin Monomethyl Ether*.—A mixture of *iso*benzalizarin (0·3 g.), methyl alcohol (20 c.c.), and methyl iodide (8 c.c.) was boiled during 8 hours, caustic potash (0·2 g.) * in methyl alcohol being gradually added. The crystals produced were washed with hot dilute hydrochloric acid to decompose a potassium salt present and crystallised from much alcohol, giving deep yellow needles (0·186 g.), m. p. 196—198° (Found : C, 78·2; H, 4·15; CH_3, 5·17. $C_{18}H_{12}O_3$ requires C, 78·3; H, 4·3; CH_3, 5·4%).

The mother-liquor contained a small amount of the same compound, but the presence of a more highly methylated product could not be detected.

By prolonged digestion with acetic anhydride and pyridine the trace of *iso*benzalizarin methyl ether available gave an *acetyl* compound which crystallised in yellow needles, m. p. about 178—180°.

*iso*Benzalizarin dyes mordanted woollen cloth shades which are very distinct from those given by benzalizarin.

	Chromium.	Aluminium.	Tin.	Iron.
*iso*Benzalizarin.	Brownish-yellow.	Greenish-yellow.	Pale yellow.	Brown.
Benzalizarin.	Brownish-maroon.	Dull reddish-orange.	Bright orange.	Brownish-black.

Anthrapurpurin Dimethyl Ether.—Triacetylanthrapurpurin (5 g.) was methylated as in the preparation of alizarin 2-methyl ether (*vide supra*), 37 c.c. of methyl sulphate and 185 c.c. of caustic soda solution being used in all. After removal of the anthrapurpurin trimethyl ether present, and crystallisation from benzene, the *dimethyl ether* was obtained in orange-red needles, m. p. 234—235°

* Approximately 2¼ times the quantity required for the production of a dimethyl ether.

(Found : C, 67·9; H, 4·2; CH_3, 10·4. $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2; CH_3, 10·6%).

The *acetyl* compound forms yellow needles, m. p. 204—205°.

Anthrapurpurinanthranol Dimethyl Ether.—A mixture of anthrapurpurin dimethyl ether (5 g.), stannous chloride (50 g.), and 30% hydrochloric acid (250 c.c.), boiled for 1¼ hours, yielded a black, granular mass, which was collected, washed with dilute hydrochloric acid, and dried. The product dissolved in alcohol was poured into ether, the precipitated amorphous impurity removed, the clear liquid evaporated, and the sandy residue washed with acetone until colourless. This on digestion with acetic anhydride and pyridine yielded *diacetylanthrapurpurinanthranol dimethyl ether*, which crystallised from alcohol–acetic acid in colourless needles, m. p. 178° (Found : C, 69·6; H, 5·0. $C_{20}H_{18}O_6$ requires C, 67·8; H, 5·1%).

The authors are much indebted to the British Alizarine Co. Ltd. for the alizarin and anthrapurpurin used in this investigation.

THE UNIVERSITY, LEEDS. [*Received, August 15th,* 1925.]

CCCLXVIII.—*Studies with the Microbalance. Part II. The Photochemical Decomposition of Silver Chloride.*

By ERNEST JOHANNES HARTUNG.

THE investigation of the action of light on silver chloride by gravimetric methods has not hitherto given very definite results. It is well known that the halide loses chlorine and diminishes in weight when insolated, but the changes are usually insignificant and afford little evidence as to the nature of the products of the action. Baker (J., 1892, **61**, 728) tried to analyse the dark photochloride produced when 51 g. of silver chloride were insolated with repeated shaking, but only 14 mg. of chlorine were evolved after considerable exposure to light. Richardson (J., 1891, **59**, 536) found 8% of the total halogen to be freed when 26 g. of silver chloride under water were insolated, but Koch and Schrader (*Z. Physik*, 1921, **6**, 127), using extremely small amounts of the dry substance, could not detect greater changes in weight than 1 or 2%. A preliminary test carried out by the author with the microbalance (J., 1922, **121**, 688) showed that a very thin film of the halide weighing 0·0880 mg. lost 81% of its total chlorine when insolated for 12 days in a vacuum. This line of attack was therefore promising, and the results of an extended investigation are now given. The Steele-Grant microbalance

employed carried a load of 105 mg. and was sensitive to 2×10^{-5} mg.; it was used in ideal conditions in a roomy cellar and had been thoroughly tested for 2 years. The weighings with this instrument are recorded to the nearest 10^{-4} mg. and they are thoroughly trustworthy to this degree of precision, for small discrepancies, in every case where they were noted, could be traced to the inevitable errors of manipulation and were never due to inaccuracy of the balance. The general plan of the work was similar to that used for the case of silver bromide (J., 1924, **125**, 2198); very thin films of the chloride on vitreous silica sheets were sealed up in glass vessels containing suitable chlorine absorbents and insolated for definite periods. The films were then weighed again and finally tested in various ways. Some experiments have also been made on the rate of chlorination of thin films of silver, and of the product of insolation of silver chloride.

Preparation of Films of Pure Silver Chloride.—Films of pure silver on vitreous silica were made by chemical deposition and subsequent ignition at 400° as already described (*loc. cit.*). These films were then chlorinated by exposure to dilute chlorine, which was made in the usual way from manganese dioxide and hydrochloric acid, followed by washing with water and drying with concentrated sulphuric acid. The rate of chlorination was comparatively slow unless the gas was dilute and the weight of the resulting silver chloride usually agreed closely with that calculated from the weight of silver taken. The maximum divergence was 1 part in 240 parts and the average was 1 part in 1400 parts. These results are distinctly less consistent than those obtained previously with silver bromide, where the maximum divergence was 1 part in 1000 parts and the average, 1 part in 2400 parts. Indeed, the whole process of chlorination of silver exhibited peculiarities which have not been observed in bromination. For example, a certain optimum concentration of chlorine in mixtures with air was found, at which addition of the halogen to silver occurred most easily, and the speed of chlorination rapidly diminished as the chlorine concentration became greater than this optimum. Also, chlorine which was made from bleaching powder and dilute sulphuric acid gave chlorinated films in which the added halogen was from 3 to 4% in excess of that required to form silver chloride. The excess could be removed by cautious heating at 200° and could be prevented by igniting the chlorine before use, This pointed to some oxygen compound as the cause, which supposition was strengthened by finding that mixtures of chlorine and moist air which had stood for some days had a tendency to give slightly high results in chlorinating silver, and that intermittent chlorination of silver films gave high results also. These effects were not noticed

in the bromination of silver; in any case, the discrepancies are small, but their reality was established by repeated tests.

Photochemical Decomposition of Silver Chloride.—The glass apparatus in which the films were sealed up and insolated was essentially similar to that used for silver bromide, and has already been described. The technique adopted was similar also, but great care was required to prevent contamination of the film by flame gases during the sealing, for silver chloride seemed to be more sensitive in this respect than the bromide. With proper precautions, however, the operation could be performed without appreciable change in weight of the film. Before exhaustion, the glass vessel was filled with air, nitrogen or hydrogen which had been carefully purified, dried and filtered before admission. The final pressure in the apparatus was usually either 10 mm. or 0·001 mm., but, as heating of the glass during exhaustion was inadmissible, the latter pressure especially was not maintained over the whole period of insolation, owing to the liberation of adsorbed gas from the glass. For this reason, the term " residual " is used in Table I to describe the conditions when the pressure of the experimental gas in the apparatus was 0·001 mm. at the time of sealing off from the pump. Copper was used as chlorine absorbent, but if insolation were performed with hydrogen present in other than residual amount, solid sodium hydroxide was substituted. Insolation was performed on the roof of the laboratory and, as the colour, opacity, and reflecting power of the films varied steadily, no estimate of the amount of radiant energy absorbed was possible. Nevertheless, the times of exposure in days afford an approximate measure of the relative amounts of energy received in each case. The pearly white films always darkened rapidly to dull purple or slate, which passed slowly to purple-brown; after several days, this had faded to very pale greyish-yellow and no further change was visible. Meanwhile, the copper in the side tube, which was shielded by an opaque cover, became heavily tarnished at the nearer end and subsequent analysis showed always the presence of chlorine on it. After a definite period of exposure, filtered air, nitrogen, or hydrogen was slowly admitted, and the film removed and weighed. The subsequent treatment varied; some of the exposed films were rechlorinated either in one or in several progressive operations, whilst others were used in attempts to discover the nature of the products of the photochemical decomposition.

A summary of the experimental results is shown in Table I, weights being given in milligrams.

Comparison of the results in the presence of air, nitrogen, and hydrogen discloses a striking resemblance between them, and it is

TABLE I.

Wt. of ignited silver.	Wt. of silver chloride.	Wt. of silver chloride calculated from silver.	Wt. of exposed film.	Wt. after rechlorination.	Percentage of total chlorine lost.	Days of exposure.	Chlorine absorbent.	Gas in apparatus.
0·2543	0·3365	0·3379	0·2899	0·3362	56·0	2	Cu	Air, residual
0·4180	0·5556	0·5554	0·4468	—	79·1	9	,,	,, ,,
0·2354	0·3125	0·3128	0·2472	0·3146*	84·7	11	,,	,, ,,
0·2428	0·3227	0·3226	0·2449	0·3250*	91·1	27	,,	,, ,,
0·3206	0·4247	0·4261	0·3432	—	78·3	10	,,	,, 10 mm.
0·2775	0·3690	0·3688	0·2862	0·3706*	90·5	87	,,	,, ,,
0·4117	0·5467	0·5471	0·4632	0·5486	61·9	87	,,	,, 760 mm.
0·1750	0·2326	0·2325	0·1863	—	80·4	15	,,	N_2, residual
0·1360	0·1812	0·1807	0·1406	0·1829	89·9	88	,,	,, ,,
0·2113	0·2809	0·2808	0·2219	—	84·4	12	,,	,, 10 mm.
0·2634	0·3496	0·3500	0·2828	—	77·5	10	,,	H_2, residual
0·1816	0·2417	0·2413	0·1852	—	94·2	62	,,	,, ,,
0·2204	0·2937	0·2929	0·2375	—	76·7	10	NaOH	,, 10 mm.
0·2108	0·2808	0·2801	0·2172	0·2820*	90·9	91	,,	,, ,,
0·2305	0·3068	0·3063	0·2466	—	78·9	10	,,	,, 760 mm.
0·1641	0·2181	0·2181	0·1669	0·2185	94·8	111	,,	,, ,,

* Chlorination in steps.

evident that oxygen is not necessary for the photochemical decomposition of silver chloride. The experiments with air in the apparatus exhibit plainly the diminution in the speed of decomposition as the gas pressure rises, due to the adverse effect of adsorbed gas films. For nitrogen, the data are insufficient to warrant conclusions being drawn, and for hydrogen, the gas pressure appears to exert little influence on the change. This behaviour is not surprising, for hydrogen acts as a sensitiser in virtue of its power of combining with chlorine under the influence of light. As in the case of the bromide, the figures indicate that the products of the photochemical decomposition of silver chloride are silver and halogen, although the final few units % of the latter are held tenaciously in the film. There is no evidence of the formation of any sub-chloride.

On rechlorinating the product of insolation, colour changes were observed similar to those seen on insolation, but in the reverse order. Eventually, the films regained their original pearly whiteness and were then usually rather heavier than in the former unexposed condition. This behaviour was always most marked when the chlorination had taken place in steps, with interruptions for the purpose of weighing, and it is believed to be due to slight oxidation during the addition of the halogen but not at other times. It was also observed to some extent when pure silver was chlorinated pro-

gressively. Hence it is probable that the figures given in Table I for the percentage of chlorine lost on insolation are not appreciably affected by oxidation due to exposure to air before weighing. Chemical analysis of the insolated material would be decisive but, with less than 0·5 mg. available in each case, no accurate procedure has yet been devised. Two simple methods were tried and neither proved to be quite satisfactory. In the first method, the film was treated with aqueous sodium thiosulphate to dissolve any unchanged silver chloride, but in spite of the greatest care insoluble particles became detached when the solution touched the film and a quantitative estimation was impossible. Much of the residue remained adherent to the silica, however, and chlorination tests proved it to be practically pure silver. In the second method, the insolated film was exposed to the vapour of purified iodine at room temperature (partial pressure 0·3 mm.) in the hope that the free silver presumably present would be attacked by the iodine to form silver iodide, the amount of which could be measured by the increase in weight. In principle, this is obviously a more rigorous means of testing the nature of the insolated film than by chlorinating it. Unfortunately, however, silver chloride itself was shown to be attacked by iodine vapour, although the complete conversion into silver iodide of even very thin films of the chloride took several days. When insolated silver chloride was exposed to the iodine vapour, the film rapidly darkened and then steadily changed to the pale yellow colour of silver iodide in about 15 minutes. The first stage of the action was now taken to be complete and the film was weighed. Table II summarises the results, weights being given in milligrams.

TABLE II.

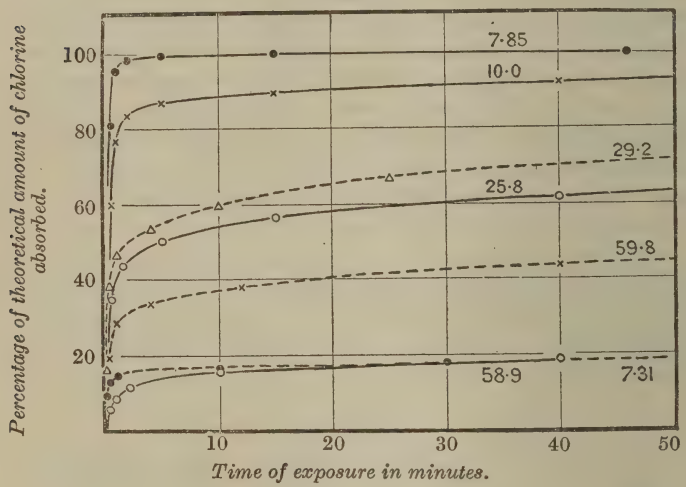
Wt. of original film.	Wt. of insolated film.	Wt. after iodination.	Wt. calculated for mixed AgI and AgCl.
0·2326	0·1863	0·3646	0·3520
0·2417	0·1852	0·3898	0·3874
0·2809	0·2219	0·4338	0·4331
0·2937	0·2375	0·4459	0·4386

The weight of the iodinated film in each case is greater than that calculated on the assumption that the insolated material is a mixture of silver and unchanged silver chloride, of which only the former is attacked by the iodine. In two instances, the discrepancy is less than 1%, and, on the whole, the results are favourable to the hypothesis mentioned, for further iodination caused steady increase in weight in each case until, after some days, all the chlorine had been displaced by iodine. The method is therefore not thoroughly sound, for the initial stages in the displacement of the chlorine proceed appreciably in a very few minutes and may, of course, be

more rapid with previously insolated films than with pure silver chloride.

Rate of Chlorination of Silver Films.—Further evidence as to the nature of insolated silver chloride was obtained by comparing the rates of addition of chlorine to pure silver and to the insolated films under the same conditions. The apparatus and methods of experiment were essentially analogous to those used in the bromination of silver (J., 1924, **125**, 2204), and have already been described. The tests were carried out in a thermostat at 25° (regulated to 0·1°) with mixtures of chlorine and air in various proportions in the chlorinating vessel. The concentration of the halogen was estimated by absorption in sodium hydroxide and titration in the usual way with

FIG. 1.



sodium thiosulphate. In every case, the total area of the film was 364 sq. mm. and the average thickness 0·00015 mm.

These results are shown graphically in Fig. 1, where the chlorine absorbed by the film, as percentage of that necessary to form pure silver chloride in each case, is plotted against total time of chlorination in minutes. The broken lines indicate rechlorination of previously insolated silver chloride films and the numbers denote chlorine concentrations in the gas phase in mg.-atoms per litre. The curves are continuous and show no irregularities which might point to the transient formation of sub-chlorides in the film. Also the remarkable fact is disclosed that the speed of chlorination of pure silver rapidly diminishes as the concentration of the halogen in the surrounding medium increases. This effect was not noticed in the bromination

of silver (*loc. cit.*), but much smaller halogen concentrations were then employed, owing to the very rapid attack of the silver films by bromine vapour. It is evident that an optimum concentration must exist at which chlorine attacks silver most readily. The precise value of this concentration has not been measured, and it is hoped to investigate the whole action thoroughly in the near future. For the present purpose, it was sufficient to show that isolated silver chloride films exhibited the same behaviour as silver itself when exposed to chlorine. That this is so will be evident from an inspection of the broken curves in Fig. 1; the existence of the optimum in this case also has been established by repeated tests, and furnishes strong evidence that silver is present in the insolated material. It cannot be there in the same form as ordinary metallic silver, however, for the optimum chlorine concentration for the product of insolation is much greater than that for the metal itself, whilst the whole rate of chlorination is comparatively very much slower for small concentrations of the halogen. In this respect, chlorine stands in marked contrast to bromine and iodine, both of which, even in small concentration, attack the product of insolation of silver chloride very rapidly.

The work described in this paper does not contradict the conclusions of Baker (J., 1892, **61**, 728) that perfectly dry silver chloride is unaffected by light and that perfectly dry chlorine will not attack silver. Owing to the danger of injuring the photosensitive films, it was not possible to bake out the glass exposing vessels, and the presence of phosphorus pentoxide has been found to be most objectionable because of the fine dust which arises from it with changes of pressure. Also, in the chlorination experiments, the halogen was "dried" with concentrated sulphuric acid only and little alteration in the results was noted when moist chlorine was substituted for it.

Summary.

1. The photochemical decomposition of silver chloride in air, nitrogen and hydrogen has been investigated by means of the microbalance.

2. The maximum percentage loss of the total chlorine in thin films of silver chloride when insolated was found to be: in air 91·1%, in nitrogen 89·9%, and in hydrogen 94·8%.

3. Evidence is adduced to prove that the photochemical decomposition products of silver chloride are silver and chlorine, and that oxygen is not necessary for the action.

4. The rates of chlorination of silver and of previously insolated silver chloride have been studied and it has been shown that optimum concentrations of the halogen exist in each case, at which the

chlorination is most rapid and above which the speed of reaction rapidly diminishes with increasing chlorine concentration.

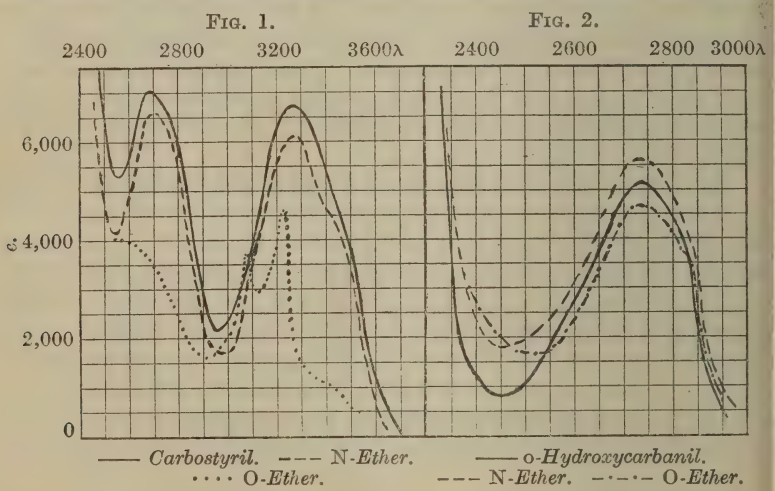
5. No evidence of the formation of silver sub-chlorides has been found.

UNIVERSITY OF MELBOURNE. [*Received, June 24th,* 1925.]

CCCLXIX.—*Absorption Spectra and Lactam–Lactim Tautomerism.*

By RICHARD ALAN MORTON and EDWARD ROGERS.

IT was assumed by the earlier workers in absorption spectra that compounds of similar constitution would show similar absorption



curves. Accordingly, in order to decide between alternative structures of a substance it was only necessary to compare its absorption spectrum with those of two derivatives of known constitution; if the general shape of its absorption curve was similar to that of a derivative, the two substances had analogous structures. In the hands of Hartley and Dobbie (J., 1899, **75**, 640) this method of interpreting absorption spectra led to conclusions in the case of lactam–lactim isomerides which are very generally quoted as establishing the value of absorption spectra in organic chemistry. These workers examined isatin, carbostyril, and *o*-hydroxycarbanil together with their *O*- and *N*-ethers; in each case the absorption spectrum of the parent substance resembled that of the lactam ether.

An examination of the published curves shows that the frequencies of maximum absorption are nearly the same for lactam and lactim isomerides in all three cases. It is agreed by all present-day workers in the field of absorption spectra that the wave-lengths of maximum absorption are of great importance in the interpretation of data. Certain authorities, notably Baly and Henri, attach fundamental importance to these frequencies as a basis for the interpretation of absorption spectra in terms of the quantum theory.

Accordingly, the fact that the shape of curves is not regarded as a trustworthy guide to interpretation, coupled with the decided advantages enjoyed by present-day workers over the pioneers in respect of technique, made it seem worth while to repeat the work of Hartley and Dobbie.

Isatin was found by Hartley and Dobbie to show two bands. Hicks (this vol., p. 774) found four bands. At the time when Hicks' paper appeared the present work had been completed and only three bands had been found. Subsequent search has not disclosed the fourth band. The three bands are at 4130Å., *e* (max.) 625; 2950Å., *e* (max.) 3,900; 2430Å., *e* (max.) 26,000 (for graph, see Hicks, *loc. cit.*, p. 771).

ψ-Methylisatin (*N*-ether), like the parent substance, shows three bands at 2465Å., 3000Å., and 4195Å. The curve follows that of isatin very closely.

Methylisatin (*O*-ether), examined as soon as possible after preparation in the pure state, shows three bands at 2447Å., 2965Å., 4140Å. The curve again follows closely that of isatin.

5-*Iodoisatin* exists in two forms, red and yellow. The red form in alcohol shows two bands, 2500 and 4250Å., with an inflexion near 3030Å., the extinctions being 25,000, 510, and 2000 (*ca.*), respectively. In glacial acetic acid, the band at 4245Å. was observed for the red form and an inflexion near 3000Å., but on account of absorption by the acetic acid the band at 2500Å. could not be observed. In a fresh solution of the yellow form there is little selective absorption, but after some time the bands due to the red form appear. Hicks records another band for iodoisatin in the extreme ultra-violet. In neither isatin nor iodoisatin can we confirm the fourth band.

A revision of the work of Hartley and Dobbie proves disappointing, for the curves are so much alike as to preclude the possibility of deciding questions of structure from them. The absorption spectra of the isomerides are nearly identical.

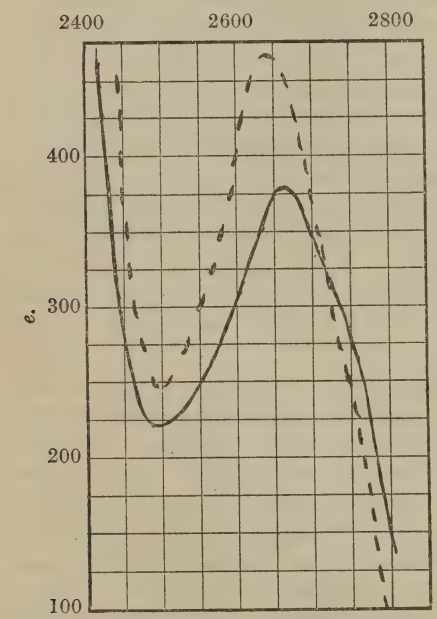
Carbostyril shows two bands at 2690Å. and 3270Å., *e* (max.) 7000 and 6750, respectively. The *N*-methyl ether has bands at 2705Å, and 3280Å., *e* (max.) 6600 and 6000, respectively. The

curves are almost identical, in agreement with the work of Hartley and Dobbie.

The *O*-methyl and *O*-ethyl ethers are almost identical as regards absorption, but are quite different from either the *N*-ether or the parent substance: *O*-Methyl ether: 3222 and 3085Å., *e* (max.) at 4500 and 3700, respectively; *O*-ethyl ether: 3226 and 3085Å., *e* (max.) at 4500 and 3700, respectively.

Both *O*-ethers show a pronounced inflexion near 2650Å. The analogous band in the parent substance and the *N*-ether has thus almost disappeared. The results confirm the *conclusions* of Hartley and Dobbie, but the experimental basis is different, since the curve for the *O*-ether is different from that of these authors.

Fig. 3.



——— *Phloroglucinol.* – – – *Trimethyl ether.*

o-*Hydroxycarbanil* shows one band with its head at 2736Å., *e* (max.) 5150.

The *N*-ether shows one band at 2738Å., *e* (max.) 5600, and the *O*-ether one at 2735Å., *e* (max.) 4700.

The curves are not very different from those of Hartley and Dobbie. The only difference observed between these substances was in respect of the persistence of the bands.

Revision of the work leads to the conclusion that the curves do not warrant any claim to discriminate between the alternative structures for *o*-hydroxycarbanil.

Phloroglucinol also has been examined, together with its trimethyl ether.

Phloroglucinol shows the following results:

Solvent.	λ max.	*e* max.	Solvent.	λ max.	*e* max.
Alcohol	2665 Å	380	Aqueous acetic acid	2660 Å	375
Water	2662	370	Alcohol with sodium		
Glacial acetic acid	2660	375	ethoxide	2518	15,200
			Ditto in excess.....	3472	6,600

Phloroglucinol trimethyl ether shows one band at 2646Å., ε (max.) 465.

The results are therefore in harmony with the accepted hydroxy-structure of phloroglucinol.

Conclusions.

In the cases of isatin and *o*-hydroxycarbanil the work of Hartley and Dobbie is unsatisfactory. Revision shows that absorption spectra do not provide any very obvious means of deciding the structure.

In the cases of phloroglucinol and carbostyril repetition of the work does not controvert the conclusions of these authors.

It may be asserted that, in general, conclusions based on the shape of absorption curves need careful examination before reliance can be placed on them.

Absorption spectra measurements should be interpreted by quantitative considerations concerning frequencies of maximum absorption. The present work will be discussed from this point of view at a later date.

We wish to express our gratitude to Professor E. C. C. Baly, F.R.S., for the interest he has taken in the work. One of us (E. R.) is indebted to the Department of Scientific and Industrial Research for a maintenance grant.

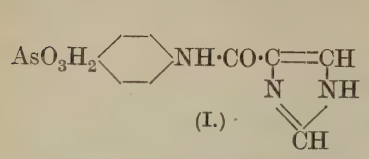
THE UNIVERSITY, LIVERPOOL. [*Received, July 9th,* 1925.]

CCCLXX.—*Trypanocidal Action and Chemical Constitution. Part III. Arsinic Acids Containing the Glyoxaline Nucleus.*

By ISIDORE ELKANAH BALABAN and HAROLD KING.

IN Part I of this series (J., 1924, **125**, 2595) it was shown that the three isomeric monoaminobenzoyl derivatives of 4-aminophenylarsinic acid showed some trypanocidal activity when tested on experimental trypanosomiasis in mice, but were not permanently curative. In Part II (this vol., p. 2632), it was shown that permanent curative properties appeared when a methoxy-group was present in the para-position in the benzoyl group in the monoaminoarsinic acids, or when there were two amino-groups present, one in each nucleus. It was therefore thought of interest to prepare *glyoxaline*-4′(or 5′)-*carboxy*-p-*aminophenylarsinic acid* (I) and its

3-*amino*-derivative (II), both of which would resemble in build and amphoteric character the amides mentioned above. It was hoped



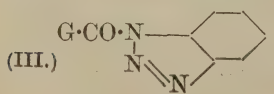
that the presence of the glyoxaline nucleus would lead to a more favourable—as regards the trypanocidal action—distribution of the amides in the tissues, especially as the glyoxaline nucleus is contained in or associated with certain substances of remarkable physiological activity such as histamine, insulin, and the pituitary active principles. Both these arsinic acids have been prepared, the first by application of the Bart-Schmidt reaction to *glyoxaline*-4(or 5)-*carboxy*-p-*aminoanilide* and the second by nitration and subsequent reduction of the parent arsinic acid.

The maximum dose tolerated by mice and the minimum curative dose on an experimental infection of *Trypanosoma equiperdum* in mice, expressed in milligrams per gram of mouse, of these two glyoxaline arsinic acids as compared with 3′-aminobenzoyl- and 3 : 3′-diaminobenzoyl-*p*-aminophenylarsinic acids is shown below,

	I.	II.	3′-NH_2.	3 : 3′-diNH_2.
Dosis tolerata	1·25	3·0	0·6	>3·5
Dosis curativa	0·8	1·5	0·3	2·0
			($r = 7$)	

r signifying the number of days the blood stream remains free from parasites. It will be observed that glyoxaline-4′(or 5′)-carboxy-*p*-aminophenylarsinic acid (I), unlike 3′-aminobenzoyl-*p*-aminophenylarsinic acid, has permanent curative properties and the enhanced curative properties of 3 : 3′-diaminobenzoyl-*p*-aminophenylarsinic acid are surpassed in 3-aminoglyoxaline-4′(or 5′)-carboxy-*p*-aminophenylarsinic acid (II).

Glyoxaline-4′(or 5′)-carboxy-*o*-aminophenylarsinic acid, isomeric with the above described para-derivative, cannot be prepared by the application of the Bart-Schmidt reaction to *glyoxaline*-4(or 5)-*carboxy*-o-*aminoanilide*, because treatment with nitrous acid gives rise to a crystalline *diazoimide* (III). In the same way the amino-arsinic acid (II) gives rise to the crystalline *diazoimide* (IV).

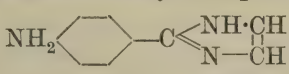


(G = glyoxalinyl)



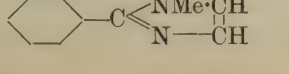
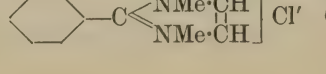
Neither of these substances couples with alkaline β-naphthol; their constitution follows from the exact analogy of their formation with Bössneck's 4-acetyl-3 : 4-tolylenediazoimide, the constitution of which was elucidated by Morgan and Micklethwait (J., 1913, **103**, 1394). The diazoimide (III) is of especial interest, because its formation will serve to detect nitrous acid as a crystalline derivative at a dilution of 1 in 6400.

In the above derivatives the glyoxaline nucleus is joined to the phenyl nucleus by an amide link. The researches of Pyman and his associates have rendered available five isomeric nitrophenylglyoxalines, without an intermediate chain of atoms. These have now been reduced to the corresponding amino-derivatives and submitted to the Bart-Schmidt process for introducing the arsinic acid group. 2-m-*Aminophenylglyoxaline* and 2-p-*aminophenylglyoxaline* (V) so prepared give no recognisable trace of arsinic acids under a variety of experimental conditions.

(V.)   (VI.)

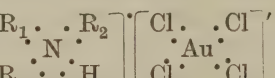
This result may be paralleled with Schmidt's inability (*Annalen*, 1920, **421**, 168) to replace the amino-group in *p*-aminodiphenyl (VI) by the arsinic acid group, although *o*-aminodiphenyl gives a 60% yield of the arsinic acid by the same reaction (Aeschlimann, Lees, McCleland, and Nicklin, this vol., p. 68). This difficulty in the case of substances containing the glyoxaline nucleus is clearly due to the fact that the most favourable conditions for carrying out the Bart-Schmidt reaction—neutrality or weak alkalinity—are precisely those which lead to coupling, internal or otherwise, of the glyoxaline nucleus present with the diazotised base. This is plainly shown, in several of the cases tried, by the concomitant separation of insoluble, highly coloured, amorphous, presumably azo-compounds.

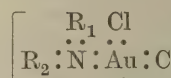
The marked change of physical properties associated with *N*-methylation of glyoxalines led to the preparation of 2-*p-nitrophenyl*-1-*methylglyoxaline* with a view to its reduction and subsequent treatment by the Bart-Schmidt reaction. The poor yield of monomethylated product, however, led us to abandon the scheme. Another avenue of approach suggested itself in the prior methylation of 2-phenylglyoxaline followed by nitration, reduction and indirect arsination. Here again the yield of monomethylated product (VII) was only 18%, the main product apart from unchanged material being 2-*phenyl*-1-*methylglyoxaline methochloride* (VIII).

(VII.)   (VIII.)

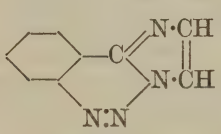
which, although the salt of a quaternary base, is precipitated as an oil on addition of strong alkali to its aqueous solutions.

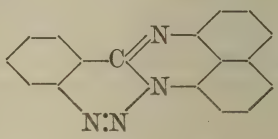
2-*Phenyl*-1-*methylglyoxaline* (VII), which is also formed by dry distillation of the methochloride (VIII) under reduced pressure, forms an abnormal *gold* salt by crystallisation of the precipitate it yields with chloroauric acid, from water containing a little acetone. The constitution of this modified gold salt, $RAuCl_3$, is similar to that of several others which have been described. The two types are readily interpreted on the electronic basis. The normal salts have the structure (IX) analogous to ammonium salts, whilst the abnormal have the structure (X) analogous to that of trimethylamine oxide.

(IX.) 

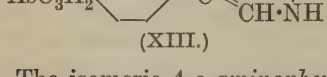

(X.)

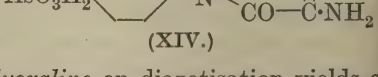
2-o-*Aminophenylglyoxaline* reacts with nitrous acid with production of a crystalline tricyclic 1 : 2 : 3-*triazine* (XI), which does not couple with alkaline β-naphthol, in exactly the same way as *o*-aminophenylperimidine yields the triazine (XII) (Sachs and Steiner, *Ber.*, 1909, **42**, 3675).

(XI.) 


(XII.)

4-p-*Aminophenylglyoxaline* submitted to the Bart-Schmidt reaction yields a very small amount of 4-*phenylglyoxaline*-p-*arsinic acid*, the main product being a purple dyestuff. The arsinic acid was not obtained in sufficient quantity for trial on experimental trypanosomiasis. This was unfortunate, as its structure (XIII) bears a close resemblance to the pyrazolone (XIV), derivatives of which are at present on the market for the treatment of protozoal diseases.


(XIII.)


(XIV.)

The isomeric 4-o-*aminophenylglyoxaline* on diazotisation yields a non-coupling, yellow *triazine* structurally related to (XI). The chief interest, however, in 4-*o*-aminophenylglyoxaline lay in the remote possibility of its resolution into enantiomorphs. Pyman has produced a considerable body of evidence for the resemblance between glyoxaline and benzene, so that the substance under consideration, being related to diphenyl, should, if Kaufler's ideas be

applied to it, be resolvable. The other type of formula, the non-coplanar type, suggested by Kenner as an explanation to be considered in the interpretation of his results, would, in the present instance, not lead to enantiomorphs. 4-*o*-Aminophenylglyoxaline has been fractionally crystallised from water at low temperatures as its *normal* d-*tartrate* and as its *dicamphor*-10-*sulphonate*, but in neither case was there any evidence of resolution.

Several attempts have been made under a variety of conditions to introduce arsenic directly into the glyoxaline nucleus, but hitherto unsuccessfully. The Béchamp reaction (heating with arsenic acid) has been applied to glyoxaline, 1-methylglyoxaline, 2-phenyl- and 4-phenyl-glyoxalines, whilst the action of arsenious chloride with or without addition of aluminium chloride has been examined on glyoxaline, 1-methylglyoxaline and 4-phenylglyoxaline.

We are much indebted to Miss F. M. Durham and Miss J. Marchal for the care exhibited in determining the therapeutic action of the arsinic acids herein described, and to Prof. Pyman, not only for freely allowing us to work in this field and for placing at our service unpublished results which materially assisted the investigation, but also for a gift of 4-*o*-nitrophenylglyoxaline.

Experimental.

Nitration of Glyoxaline-4(or 5)-*carboxyanilide*.—The nitrate separating from water is dimorphous, both forms crystallising with $\frac{1}{2}H_2O$, (*a*) unstable, fluffy needles, loss at 100° = 4·3; (*b*) stable, stout prisms, m. p. 170—171° (decomp.), loss at 100° = 3·4: Theory for $\frac{1}{2}H_2O$ = 3·5%. Found in dry salt by nitron estimation, HNO_3, 25·1 (Theory requires HNO_3, 25·2%). The nitrate (75 g.) was added gradually and with ice-cooling to 150 c.c. of concentrated sulphuric acid. The product was kept for 3 hours at room temperature and then poured into ice-water; the solid obtained (55·5 g.), m. p. 265° (decomp.), recrystallised twice from 700 c.c. of *N*-hydrochloric acid, gave 33·8 g. of *glyoxaline*-4(or 5)-*carboxy*-p-*nitroanilide hydrochloride*. A further 4·7 g. were obtained from the mother-liquors.

The sulphuric acid mother-liquors were heated at 80° and fractionally precipitated by addition of sufficient strong alkali to produce a slight separation of solid from the hot solution and copious crystallisation when cold. The process was repeated until all acidity was removed, final neutralisation being effected by saturated sodium carbonate. Several crops of almost pure *glyoxaline*-4(or 5)-*carboxy*-o-*nitroanilide*, m. p. 229°, were thus obtained. This was finally purified as hydrochloride. The final mother-liquors of the fractionation gave 1·0 g. of *p*-nitroaniline (m. p. 147°).

In all, 38·5 g. of the *p*-isomeride and 15·4 g. of the *o*-isomeride were obtained in a pure state as hydrochlorides, yields of 36 and 14·3% respectively.

Glyoxaline-4(or 5)-*carboxy*-p-*nitroanilide hydrochloride monohydrate* crystallises from *N*-hydrochloric acid, in which it is sparingly soluble, in long, colourless, rectangular prisms or tablets decomposing about 298°. It also crystallises in fluffy needles which, on standing in contact with the solution, pass into the previously described stable variety (Found : loss at 95°, 1·9; Cl, 12·4. $C_{10}H_8O_3N_4$,HCl,H_2O requires Cl, 12·4%. When dried at 110°, the salt suffers complete loss of water and partial loss of hydrogen chloride. Found : loss, 7·4; Cl, 12·1. The monohydrate requires H_2O, 6·3%. $C_{10}H_8O_3N_4$,HCl requires Cl, 13·2%).

The *base* crystallises from glacial acetic acid in long, colourless plates, m. p. 307° (corr.), which contain two mols. of acetic acid (Found : loss at 95°, 37·1; on dried solid, C, 51·7; H, 3·5. $C_{10}H_8O_3N_4$,$2C_2H_4O_2$ requires loss, 34·1%. $C_{10}H_8O_3N_4$ requires C, 51·7; H, 3·4%). It is practically insoluble in water and the usual organic solvents except acetic acid. It dissolves in 2*N*-sodium hydroxide with a pale yellow colour and is reprecipitated by carbon dioxide. It forms a sparingly soluble *nitrate*, m. p. 205° (decomp.).

Glyoxaline-4(or 5)-*carboxy*-o-*nitroanilide* crystallises from glacial acetic acid in bright yellow, glistening plates, m. p. 229° (Found : C, 51·3; H, 3·5. $C_{10}H_8O_3N_4$ requires C, 51·7; H, 3·4%). It is practically insoluble in water and the usual organic solvents except acetic acid. In 2*N*-sodium hydroxide it dissolves with an intense yellow colour and is precipitated by carbon dioxide as glistening, yellow needles. The *nitrate*, from 2*N*-nitric acid, crystallises in long, yellow prisms, m. p. 196° (decomp.). The *hydrochloride* crystallises from *N*-hydrochloric acid, in which it is moderately easily soluble, in yellow, rectangular, anhydrous prisms (Found : Cl, 13·0. $C_{10}H_8O_3N_4$,HCl requires Cl, 13·2%).

Hydrolysis of the Nitro-compounds.—2·0 Grams of each hydrochloride were boiled for 3 hours with 20 c.c. of 16% hydrochloric acid. Extraction with ether isolated *p*- and *o*-nitroaniline respectively, which were identified by the melting points of mixtures with authentic specimens. The mother-liquors were partly basified; glyoxaline-4(or 5)-carboxylic acid was then isolated, effervescing at 275° (alone, or mixed with an authentic specimen).

Glyoxaline-4(or 5)-*carboxy*-p-*aminoanilide Dihydrochloride.*—Twelve grams of the hydrochloride of the *p*-nitroanilide were added to a mixture of 75 c.c. of concentrated hydrochloric acid and 75 c.c. of alcohol containing 30 g. of hydrated stannous chloride in solution. On heating at 80°, a bulky, pale yellow precipitate separated, which

dissolved on addition of more alcohol. On cooling, 15·6 g. of the *stannichloride* of the amino-base, m. p. 290° (decomp.), separated, and a further 2·3 g. on concentration of the mother-liquors. After removal of tin as sulphide, the *dihydrochloride* of the base, 9·55 g. or 80% of theory, was isolated. This salt crystallises from dilute hydrochloric acid in colourless, glistening, rectangular prisms which blacken at about 290° and crystallise with one molecule of water (Found : loss, 6·1 ; on anhydrous salt, Cl, 25·9. $C_{10}H_{10}ON_4,2HCl,H_2O$ requires H_2O, 6·1%. $C_{10}H_{10}ON_4,2HCl$ requires Cl, 25·8%). The diazotised salt couples with alkaline β-naphthol with production of a red solution. The *base* is precipitated by addition of sodium carbonate solution. It is moderately soluble in water and crystallises in colourless, glistening, delicate plates, m. p. 228°. The *picrate* crystallises in long, fine, yellow needles darkening at 256° and decomposing at 266°, and is very sparingly soluble in boiling water (Found : H_2O, 5·7 ; on dried salt, picric acid, estimated by nitron, 53·0. $C_{10}H_{10}ON_4,C_6H_3O_7N_3,1\frac{1}{2}H_2O$ requires H_2O, 5·9%. $C_{10}H_{10}ON_4,C_6H_3O_7N_3$ requires picric acid, 53·1%).

Glyoxaline-4(or 5)-*carboxy*-o-*aminoanilide Dihydrochloride*.—Six grams of the hydrochloride of the nitroanilide were reduced in the same way as the *p*-nitroanilide. On keeping, the *stannichloride* (11·0 g.) separated in colourless, rectangular prisms, and on concentration another 2·0 g. were obtained. On removal of tin as sulphide and concentration to a low bulk, *glyoxalinecarboxy*-o-*aminoanilide dihydrochloride* crystallised out (yield 5·4 g. or 87·5%). This salt crystallises from dilute hydrochloric acid in long, rectangular prisms which decompose at 310° and crystallise with one-half a molecule of water (Found : loss at 100°, 3·6. $C_{10}H_{10}ON_4,2HCl,\frac{1}{2}H_2O$ requires H_2O, 3·2%. Found : on dried salt, Cl, 25·5. $C_{10}H_{10}ON_4,2HCl$ requires Cl, 25·8%). It is very readily soluble in water and on addition of sodium nitrite a *diazoimide* (III) crystallises out. This is sparingly soluble in boiling acetic acid, ethyl alcohol or benzene, somewhat more readily soluble in boiling methyl alcohol, from which it separates in fine needles, m. p. 195—196°, but varying with the rate of heating. The diazoimide is soluble in sodium hydroxide solution but not in sodium carbonate, and forms an insoluble hydrochloride with concentrated hydrochloric acid, but dissolves on dilution. It produces no colour on addition to alkaline β-naphthol solution. It is very sparingly soluble in water and will detect nitrous acid as a solid crystalline derivative at a dilution of 1 in 6400 in the presence of sodium acetate, or, conversely, the anilide can be detected at a dilution of 1 in 5000.

The *amino-base* is precipitated on careful addition of sodium

carbonate to the dihydrochloride. It is moderately easily soluble in boiling water and crystallises in fine needles, m. p. 270° with previous darkening. The *dipicrate* is very sparingly soluble in boiling water and crystallises in minute needles, m. p. 242° (decomp.) (Found: H_2O, 5·9, 5·6; on dried salt, picric acid, 70·8, 71·0. $C_{10}H_{10}ON_4,2C_6H_3O_7N_3,2\frac{1}{2}H_2O$ requires H_2O, 5·8%.

$C_{10}H_{10}ON_4,2C_6H_3O_7N_3$

requires picric acid, 69·4%).

Glyoxaline-4'(or 5')*-carboxy*-p-*aminophenylarsinic Acid* (I).—Glyoxalinecarboxy-*p*-aminoanilide dihydrochloride (27·3 g.) (in 5 batches) was dissolved in 150 c.c. of water, cooled to 0°, and diazotised by addition of 100 c.c. of 10% sodium nitrite solution. To the clear solution 9·0 g. of arsenious oxide in 70 c.c. of 2*N*-sodium hydroxide were added to produce a faintly alkaline reaction. A light brown precipitate separated and a considerable amount of frothing took place. After keeping over-night, the solution was warmed on the water-bath and filtered from coloured by-products. The filtrate was fractionally precipitated with strong hydrochloric acid and after removal of amorphous material a crystalline crop separated. On keeping, 11·2 g. (36% yield) of crude arsinic acid were obtained. It crystallised from 75% acetic acid (50 vols.) in pale yellow, glistening, triangular leaflets which darkened at 280°. This acid is almost insoluble in boiling water or glacial acetic acid, dissolves more readily in mixtures, but is readily soluble in boiling 25% formic acid, separating in needles, forming a very stable monohydrate (Found on various samples: loss at 105°, 0·7; As, 22·4, 22·4, 22·8. $C_{10}H_{10}O_4N_3As,H_2O$ requires As, 22·8%). A 1% solution in 0·2*N*-ammonia treated with a tenth of its volume of 5% magnesium or calcium chloride gave an immediate precipitate of the *magnesium* salt in fine needles, but the *calcium* salt separated in anisotropic spheroids, only on heating. The *sodium* salt crystallises in needles, and the *hydrochloride* in fine needles.

Glyoxaline-4'(or 5')*-carboxy*-p-*amino-3-nitrophenylarsinic Acid*.—Glyoxalinecarboxy-*p*-aminophenylarsinic acid (9·9 g.) was dissolved in 30 c.c of sulphuric acid at 0° and nitrated by addition of 3 g. of nitric acid (*d* 1·42) dissolved in a few c.c. of sulphuric acid. When the mixture was poured on to ice, the crude nitro-acid (10·5 g.) separated, at first in leaflets, but later in needles. The mother-liquors, neutralised to Congo-paper and kept at 0° for 3 days, deposited a further 2·0 g. of nitro-acid. The pure nitro-acid is best obtained by crystallisation from 50% acetic acid. It is almost insoluble in boiling water or boiling glacial acetic acid. From 25% formic acid it separates in clusters of yellow plates, m. p. about 327° (decomp.). It forms a very stable monohydrate (Found:

loss at 110°, 0·9; on two distinct samples of dried acid, As = 19·8, 19·9. $C_{10}H_9O_6N_4As,H_2O$ requires As, 20·0%). 1% Solutions in 0·2*N*-ammonia were treated with a tenth of the volume of 5% lithium, magnesium, calcium or barium chloride; a micro-crystalline precipitate of the *magnesium* salt formed immediately, the *calcium* salt separated almost immediately in fine needles, and the *barium* salt also in fine needles, especially on rubbing the walls of the vessel. The *lithium* salt separated after keeping for several days.

Hydrolysis of the Nitro-acid.—Two grams of the pure acid were boiled for 30 minutes with 30 c.c. of *N*-sodium hydroxide, and the solution was cooled and made neutral to Congo-paper. Successive crops of acids were obtained which by suitable crystallisation from water gave eventually an 86% yield of 3-nitro-4-aminophenylarsinic acid and an 83% yield of glyoxalinecarboxylic acid. There was no evidence for the presence of isomeric nitro-acids, and no definite evidence was obtained from fractional crystallisation of 10 g. of crude glyoxalinecarboxy-*p*-aminonitrophenylarsinic acid.

Glyoxaline-4′(or 5′)-*carboxy*-p-*amino*-3-*aminophenylarsinic acid* (II) was prepared by dissolving 8·0 g. of the nitro-acid in 80 c.c. of 2*N*-sodium hydroxide at − 5°, adding gradually 28 g. (7 mols.) of ferrous chloride in 40 c.c. of water and and finally 80 c.c. of 2*N*-sodium hydroxide. After filtration, the ferric hydroxide was extracted thrice with 150 c.c. of 0·2*N*-sodium hydroxide. The combined filtrates were neutralised to Congo-paper, and the crude amino-acid (5·65 g.), which separated crystalline, was collected. The mother-liquors were made alkaline with ammonia and heated with magnesium chloride. The magnesium salt which separated was dissolved in 50 c.c. of *N*-hydrochloric acid, and the acidity removed by sodium acetate. The amino-acid so obtained weighed 0·85 g. The total yield of crude amino-acid was 86%. It was purified with difficulty by dissolving in 0·5*N*-hydrochloric acid and cautiously adding saturated sodium acetate solution until the solution was only faintly acid to Congo-paper. This caused the gradual separation of a green, flocculent substance which could be filtered off; the amino-acid was precipitated from the filtrate by further addition of sodium acetate. The pure amino-acid crystallises in fine, long, colourless, rectangular prisms which are unmelted at 320°. They contain half a molecule of water, not lost at 100° (Found: As, 22·4, 22·2. $C_{10}H_{11}O_4N_4As,\frac{1}{2}H_2O$ requires As, 22·4%). In hydrochloric acid solution addition of sodium nitrite causes an immediate precipitation of a crystalline *diazoimide* (IV), which separates from dilute solutions in microscopic leaflets. The diazoimide does not couple with β-naphthol. A 1% solution of the amino-acid in 0·2*N*-ammonia treated with one-tenth its volume of

5% magnesium or calcium chloride gave an immediate precipitate of the *magnesium* salt in fine needles, whilst the *calcium* salt was precipitated, in crystalline tufts, only on heating.

2-p-*Aminophenylglyoxaline dihydrochloride* (V) was obtained by reducing 19·0 g. of 2-*p*-nitrophenylglyoxaline with 68 g. of stannous chloride in 170 c.c. of concentrated hydrochloric acid. The *stannichloride* separated, in colourless needles, after digestion on the water-bath. Its de-tinned solution, on concentration, gave 16·2 g. of the pure *dihydrochloride*, crystallising in colourless, rectangular prisms which darken at about 300° (Found: Cl, 30·5. $C_9H_9N_3,2HCl$ requires Cl, 30·6%). It diazotises and couples with alkaline β-naphthol, forming a deep red solution, and also gives an intense red solution with Pauly's reagent. The free *base* is an oil which turns brown on exposure to air. The *monopicrate* is very sparingly soluble in water and crystallises in orange, glistening, rectangular plates, decomp. about 238° (Found: picric acid by nitron, 58·7. $C_9H_9N_3,C_6H_3O_7N_3$ requires picric acid, 59·0%). Under no conditions could any arsinic acid be isolated by the application of the Bart reaction to this aminophenylglyoxaline.

Action of Methyl Sulphate on 2-p-*Nitrophenylglyoxaline*.—The base (12·6 g.) was heated at 100° with 8·4 c.c. of methyl sulphate for 1 hour. After initial liquefaction the product set to a cake. The solid obtained on treatment with sodium hydroxide was crystallised as hydrochloride; 6·0 g. of the hydrochloride of the initial material were recovered. The hydrochloride mother-liquors, on being basified, gave 1·0 g., m. p. below 120°. This was 2-p-*nitrophenyl*-1-*methylglyoxaline*, and when recrystallised from water it separated in long, pale yellow, silky needles, m. p. 116·5° (corr.). It is moderately soluble in boiling water, sparingly so in ether, and very soluble in alcohol, benzene, or chloroform. The *chloroaurate* crystallises from 3*N*-hydrochloric acid in golden-yellow, irregular prisms which decompose at 226° (corr.). It is soluble to the extent of 1 in 300 in the boiling acid (Found: Au, 36·4. $C_{10}H_9O_2N_3,HAuCl_4$ requires Au, 36·3%). The *hydrochloride* crystallises in elongated plates and is very soluble in water. The *nitrate* crystallises in diamond-shaped plates effervescing at 186° (corr.). It is moderately soluble in water, but sparingly soluble in dilute nitric acid. The *picrate* crystallises from alcohol, in which it is very sparingly soluble, in fine, glistening needles, m. p. 212° (corr.) (Found: picric acid by nitron, 53·1. $C_{10}H_9O_2N_3,C_6H_3O_7N_3$ requires picric acid, 53·0%).

2-m-*Aminophenylglyoxaline dihydrochloride* was obtained by reducing 7·0 g. of the *m*-nitrophenylglyoxaline with 25 g. of stannous chloride in 64 c.c. of concentrated hydrochloric acid and 30 c.c. of

alcohol on the water-bath. When cold, the *stannichloride* separated in rectangular prisms which, after de-tinning and concentration, gave 6·2 g. of the pure dihydrochloride. This salt is a *monohydrate* and melts with decomposition at 282°. It is very soluble in water, less soluble in acid solutions (Found: loss, 7·3; on dried salt, Cl, 30·5. $C_9H_9N_3,2HCl,H_2O$ requires H_2O, 7·3%. $C_9H_9N_3,2HCl$ requires Cl, 30·6%). After diazotisation, it couples with alkaline β-naphthol with an intense red colour. The *base* liberated by addition of sodium bicarbonate is very soluble in water. It is a *monohydrate* which partly melts with effervescence between 130 and 140° and finally melts at 202—203°. When dried at 95°, it melts at 203—204° (Found: loss at 95°, 9·1. $C_9H_9N_3,H_2O$ requires H_2O, 10·2%). The anhydrous base is sparingly soluble in boiling acetone, benzene, or ethyl acetate, and readily soluble in hot alcohol, from which it crystallises in fine needles. The *monopicrate* crystallises from water, in which it is very sparingly soluble, in long spikes, decomp. 218° (Found: picric acid by nitron, 58·0. $C_9H_9N_3,C_6H_3O_7N_3$ requires picric acid, 59·0%).

Attempts to replace the amino-group in this base by the arsinic acid group by the Bart reaction were all unsuccessful.

2-o-*Aminophenylglyoxaline dihydrochloride* was prepared from the nitro-compound by reduction with stannous chloride, the *stannichloride* separating in thin plates. The *dihydrochloride* (Found: Cl, 30·5. $C_9H_9N_3,2HCl$ requires Cl, 30·5%) crystallised in large, glassy tablets melting at 234—236° and decomposing a few degrees higher. It was readily soluble in water and on addition of sodium nitrite gave a triazine (XI) crystallising in needles, m. p. 113—114°. This triazine is insoluble in alkali, but immediately soluble in concentrated hydrochloric acid. From 3*N*-hydrochloric acid the hydrochloride of the triazine crystallises in needles. The triazine does not couple with alkaline β-naphthol. The *monopicrate* of the *o*-base is readily soluble in boiling water and crystallises in small, feathery needles, m. p. 211—212° (without decomp.) (Found: picric acid, 59·6. $C_9H_9N_3,C_6H_3O_7N_3$ requires picric acid, 59·0%). The *base* melts at 136—137° and crystallises from water in large, white, fern-like crystals.

4-p-*Aminophenylglyoxaline dihydrochloride* was prepared by reducing the *p*-nitro-base (19 g.) by 68 g. of stannous chloride in 170 c.c. of concentrated hydrochloric acid and 50 c.c. of alcohol on the water-bath at 80°. The *stannichloride* (needles darkening at 310°) crystallised from the hot solution. After removal of tin as sulphide, 17·1 g. of pure *dihydrochloride* were obtained in colourless, glistening needles which darken at 310° (Found: Cl, 30·5. $C_9H_9N_3,2HCl$ requires Cl, 30·6%). It is readily soluble in water, and when

diazotised gives with alkaline β-naphthol an intense purple dye; but a similar colour is obtained with the diazotised base and sodium hydroxide alone. It gives an intense red colour with Pauly's reagent. The *base* crystallises from water, in which it is moderately soluble, in glistening, hexagonal plates, m.p. 98° (corr.). The *dipicrate* crystallises from water, in which it is very sparingly soluble, in yellow needles, m. p. 240° (decomp.) (Found : picric acid, 73·9. $C_9H_9N_3,2C_6H_3O_7N_3$ requires picric acid, 74·2%).

Glyoxaline-4(or 5)-*phenyl*-p-*arsinic acid* (XIII) was obtained by addition of sodium nitrite to 4-*p*-aminophenylglyoxaline dihydrochloride (10 g.) at 0° and subsequent addition of 6·6 g. of arsenious oxide in 36 c.c. of 2*N*-sodium hydroxide. An intense dark purple solution was formed, but the reaction of the solution could be adjusted to neutrality by use of glazed litmus paper. When the evolution of nitrogen had ceased, the solution was warmed on the water-bath, and the insoluble dyestuff filtered off. The solution was made neutral to Congo-paper and, after removal of amorphous material, was concentrated. The arsinic acid separated in reddish-yellow plates, which were unmelted at 310° (yield 0·5 g.). On crystallisation from glacial acetic acid, it separated in dense yellowish-brown prisms. The amount of material was insufficient for analysis, but served to confirm its identity. Further experiments under a variety of conditions resulted in no improvement of the yield. This acid gave an intense reaction with Pauly's reagent. Its ammoniacal solution gave an amorphous *magnesium* salt on heating, but the *calcium* salt separated in the cold in sphærocrystals. The barium and lithium salts were soluble. From alkaline solutions the acid is precipitated by addition of mineral acid in colourless, elongated leaflets.

4-o-*Aminophenylglyoxaline dihydrochloride* was obtained by reduction of the nitro-base by stannous chloride in concentrated hydrochloric acid. On removal of tin and concentration, the *dihydrochloride monohydrate* separated in colourless prisms which effervesce at 256° and do not lose the water of crystallisation at 95° (Found : Cl, 29·1, 29·1. $C_9H_9N_3,2HCl,H_2O$ requires Cl, 29·2%). It is very soluble in water and with sodium nitrite gives a bright yellow solution from which the triazine separates in clusters of microscopic needles. It does not couple with alkaline β-naphthol and is not soluble in alkali. The *base* separates as an oil on addition of sodium hydroxide, but a slight excess of sodium bicarbonate causes it to crystallise in square plates, m. p. 131°. It is soluble in water, sparingly soluble in ether, and is unaffected by excess of sodium hydroxide. The *dipicrate* crystallises in elongated plates from water, in which it is sparingly soluble, and decomposes about 200°

(Found: picric acid by nitron, 73·5. $C_9H_9N_3,2C_6H_3O_7N_3$ requires picric acid, 74·2%). The *normal tartrate* separates in felted needles from aqueous solutions containing molecular proportions of the constituents or one molecular proportion excess of tartaric acid. Repeated crystallisation at temperatures below 40° failed to effect any change in its rotation or melting point. It crystallises with $1·5H_2O$ and loses $1H_2O$ in a vacuum over sulphuric acid. When air-dried or dried in a vacuum, it melts at 95—97° and then effervesces at about 130° [Found: loss in a vacuum, 5·3; on vacuum-dried material, C, 49·1; H, 5·1. $C_9H_9N_3,C_4H_6O_6,1\frac{1}{2}H_2O$ requires (for loss of $1H_2O$), H_2O, 5·4%. $C_9H_9N_3,C_4H_6O_6,\frac{1}{2}H_2O$ requires C, 49·1; H, 5·1%]. The specific rotation was determined in water: $c = 0·914$; $l = 2$; $\alpha + 0·27°$; $[\alpha]_{5461} + 14·8°$. The *di*-d-*camphor*-10-*sulphonate* is readily soluble in water, from which it crystallises in anhydrous needles, m. p. 198—200° (Found: S, 10·1. $C_9H_9N_3,2C_{10}H_{16}O_4S$ requires S, 10·0%). The rotation was unchanged after recrystallisation from water below 40°: $c = 1·0$; $l = 2$; $\alpha + 0·428°$; $[\alpha]_{5461} = + 21·4°$: $c = 2·04$; $l = 2$; $\alpha + 0·868°$; $[\alpha]_{5461} = + 21·3°$; whence $[M]_{5461} = 133·1°$. Graham (J., 1912, **101**, 747) gives for the molecular rotation of the camphorsulphonic ion $[M]_{5461} = 66·5$; whence, for two ions, $[M]_{5461} = 133·0°$, a value identical with that observed for the above salt.

Methylation of 2-*Phenylglyoxaline.*—Methyl sulphate (28 c.c.) was added in small quantities to 40 g. of 2-phenylglyoxaline with cooling. A vigorous reaction ensued and the mass liquefied. After heating for 30 minutes on the water-bath, the product was treated with 20 c.c. of water and mixed with sodium nitrate and nitric acid. On concentration, an oily layer separated, which deposited 11·2 g. of a nitrate, m. p. 126°; this, on recrystallisation, gave eventually 8·5 g. of unchanged 2-phenylglyoxaline, and from its mother-liquors, 1·3 g. of 2-phenylglyoxaline picrate, m. p. 234°, and 1·0 g. of a new picrate, m. p. 132°. The original nitrate mother-liquors were concentrated further, made alkaline with sodium hydroxide, and extracted with chloroform. The chloroform was extracted twice with water; the aqueous solution, on evaporation with hydrochloric acid, gave 15·5 g. of 2-*phenyl*-1-*methylglyoxaline methochloride* (VIII). The chloroform extract, distilled at 20 mm., gave 9·4 g. of an oil, b. p. 190°, from which alcoholic picric acid produced 27 g. of picrate, m. p. 124°. On recrystallisation from water, 19·2 g. of 2-*phenyl*-1-*methylglyoxaline picrate*, m. p. 132°, were obtained, and from the mother-liquors 1·6 g. of 2-phenylglyoxaline picrate, m. p. 232°, with various small crops of mixed picrates. 2-Phenylglyoxaline, 2-phenyl-1-methylglyoxaline, and

2-phenyl-1-methylglyoxaline methochloride were obtained in yields of 32·3, 18·2, and 26·7% respectively.

2-*Phenyl*-1-*methylglyoxaline* (VII) is a viscous, pale yellow oil, b. p. 175°/15 mm., with a strong but not unpleasant odour. It is not soluble in water, but soluble in organic solvents. The *chloroaurate* is practically insoluble in water, alcohol, or 3*N*-hydrochloric acid, but can be recrystallised from the first-named by addition of a little acetone. It separates in deep yellow, elongated prisms, m. p. 189° (corr.) (Found: Au, 42·8. $C_{10}H_{10}N_2,AuCl_3$ requires Au, 42·7%). The *nitrate* is a very soluble salt crystallising in needles, m. p. about 100°. The *picrate* separates from 60 parts of boiling water in glistening, elongated plates, m. p. 133° (corr.). It dissolves three times as readily in boiling alcohol (Found: picric acid, 59·3. $C_{10}H_{10}N_2,C_6H_3O_7N_3$ requires picric acid, 59·2%). The *hydrochloride* is extremely readily soluble in water or alcohol and separates in needles (Found: loss in a vacuum, 14·9; on dried material, Cl, 18·4. $C_{10}H_{10}N_2,HCl,2H_2O$ requires H_2O, 15·6%. $C_{10}H_{10}N_2,HCl$ requires Cl, 18·2%). The *hydrogen oxalate* crystallises from alcohol in colourless, long needles, m. p. 135° (corr.). It is readily soluble in water and hot alcohol [Found: N, 11·0 (Kjeldahl). $C_{10}H_{10}N_2,C_2H_2O_4$ requires N, 11·3%].

2-*Phenyl*-1-*methylglyoxaline methochloride* was obtained in small, very hygroscopic needles, m. p. 272°, by dissolution in absolute alcohol and addition of ether (Found: H, 6·2; N, 13·7; Cl, 16·7. $C_{10}H_{10}N_2,CH_3Cl$ requires H, 6·2; N, 13·4; Cl, 17·0%). On addition of strong alkali to an aqueous solution the quaternary base is precipitated as an oil. The *chloroaurate* crystallises from dilute hydrochloric acid, in which it is very sparingly soluble, in pale yellow, elongated leaflets, m. p. 134° (corr.) (Found: Au, 38·5. $C_{11}H_{13}N_2,AuCl_4$ requires Au, 38·5%).

Distillation of 2-*Phenyl*-1-*methylglyoxaline Methochloride*.—Five grams of this salt were distilled at 15 mm. 2-Phenyl-1-methylglyoxaline distilled over at 175° in 56% yield. It was converted into the picrate, m. p. 132°, and proved to be identical with that described above.

We are indebted to Mr. W. Anslow for the majority of the analyses recorded in this paper.

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CCCLXXI.—*The Rate of Reaction of Bromine with Aqueous Formic Acid.*

By Dalziel Llewellyn Hammick, William Kenneth Hutchison, and Frederick Rowlandson Snell.

Formic acid in aqueous solution is oxidised by each of the halogens to carbon dioxide and halogen acid, the reactions in the cases of bromine and iodine proceeding at rates that make velocity measurements possible. An account is now given of a study of the kinetics of the oxidation by bromine. Somewhat similar reactions have been studied by Bugarsky (*Z. physikal. Chem.*, 1901, **38**, 561; 1904, **48**, 63), who recognised clearly the disturbing effects due to the products of the reaction, to which effects further reference will be made.

That the reaction goes to completion in accordance with the equation $HCO_2H + Br_2 = 2HBr + CO_2$ was established in the following manner. A strong solution of bromine in water was contained in an apparatus as described by Richards (*ibid.*, 1902, **41**, 544) which delivered bromine solution of constant strength. The amount of bromine in one measure (about 15 c.c.) was estimated iodometrically. A mixture of exactly 20 c.c. of a solution of formic acid of known strength, 4 measures of bromine water, and 20 c.c. of approx. *N*-hydrobromic acid was kept in a thermostat at 25° for 3 days. By estimating the residual bromine it was found that 2·23 g.-mols. of formic acid react with 2·24 g.-mols. of bromine.

Materials and Method.—The bromine, prepared from pure potassium bromide, contained 99·6% Br, and no detectable iodine. The anhydrous formic acid contained 99·7% HCO_2H. A Jena glass flask, of about 450 c.c. capacity, with a narrow neck and ground glass stopper was used as the reaction vessel, placed in a thermostat at 25·00° ± 0·04°. The initial volume of reaction mixture was always 400 c.c.

Preliminary experiments established the following points: (1) Under the conditions of working, light has no appreciable effect on the rate of reaction. (2) The rate of reaction is greatly diminished by the presence of hydrogen- or bromine-ion.

Experiments were therefore made to determine the rate of disappearance of bromine in solutions containing excess of both formic acid and hydrobromic acid. Quantities of 25 c.c. of the reaction mixture were withdrawn at measured times and discharged into potassium iodide solution. The iodine liberated was then titrated with standard thiosulphate. In all these experiments the titration of the initial quantity of bromine was carried out under similar

conditions of acidity. But no attempt was made to neutralise the excess of acid in the titrations, since the form of the monomolecular velocity coefficient ensures that any proportional error in the titration will be eliminated.

Table I shows that the rate of disappearance of bromine follows the monomolecular law $k = 2{\cdot}303/t \,.\, \log\{a/(a - x)\}$, where a is the initial titre equivalent to 25 c.c. of reaction mixture and $(a - x)$ is the titre at time t (mins.). A zero time correction was introduced owing to the time of mixing being rather long compared with the time of reaction. This correction, obtained by plotting values of $\log\{a/(a - x)\}$ against t and extrapolating back to zero, was never very large, being generally of the order of $-0{\cdot}1$ min. All the values of k have been computed after the addition or subtraction of the necessary correction thus obtained.

TABLE I.

c_{HBr}, c_{HCO_2H}, and initial concentration of bromine = 0·1665, 0·278, and 0·0108 g.-mol. per litre, respectively. Zero time = −0·05 min.

t	0·00	1·82	3·30	4·32	5·68	7·30	11·80
Br titre (c.c.)	27·12	18·69	13·32	10·81	8·18	5·82	2·40
k	—	0·205	0·215	0·213	0·212	0·211	0·206
						Mean	0·210

Table II summarises the results of similar experiments carried out in order to determine the influence of the concentration of the formic acid on the rate of reaction. The value of the monomolecular velocity coefficient, $k_{Obs.}$, is the measure of the rate of the reaction, and the constancy of the quotient $k_{Obs.}/c_{HCO_2H}$ is satisfactory proof that the rate is proportional to the concentration of formic acid. The reaction between bromine and formic acid is therefore of the second order. It remained to investigate the influence of the hydrogen and bromine ions on the rate of reaction.

TABLE II.

c_{HBr} = 0·1820 g.-mol. per litre.

c_{HCO_2H}	0·1409	0·1409	0·2113	0·2818	0·4227
$k_{Obs.}$	0·092	0·096	0·146	0·192	0·284
$k_{Obs.}/c_{HCO_2H}$	0·653	0·681	0·693	0·683	0·673

Jakowkin (*Z. physikal. Chem.*, 1896, **20**, 19) and others have shown, as a result of partition experiments, that bromine in a solution containing excess of bromine ions is present largely as the tribromide ion. The equilibrium constant

$$K_1 = [Br'][Br_2]/[Br_3'] \quad . \quad . \quad . \quad . \quad . \quad (1)$$

has been calculated to about 0·063, assuming complete dissociation of the electrolytes involved. The corresponding constant for the

combination of bromine molecules with chlorine ions is of the order of 0·8. Now, in order to study the reaction at different concentrations of hydrogen ion, it is necessary to add varying quantities of some strong acid, and for this purpose hydrochloric acid appeared most suitable. But sufficient hydrobromic acid must be present, not only to maintain the bromine-ion concentration constant, but also to outweigh the much slighter influence of the chlorine ion in removing bromine molecules from the solution, and so render the disturbing effect of the chlorine ion negligible. Table III summarises the results of experiments carried out on these lines. The normality of the hydrobromic acid was 0·1213 throughout and that of the hydrochloric acid never exceeded 0·2540, so that the disturbing effect of the chlorine ion would never be serious. Under " α " are given the activity coefficients of hydrochloric acid (Lewis and Randall, " Thermodynamics," 1923, p. 336) for the total acid concentration; for since coefficients for hydrobromic acid were not available, it was assumed that they would not be very different from those for hydrochloric acid.

TABLE III.

$c_{HCO_2H} = 0{\cdot}282$ g.-mol. per litre. $c_{HBr} = 0{\cdot}1213N$.

c_{HCl} (N).	$c_{(HBr,HCl)}$ (N).	α.	$k_{Obs.}$	$\alpha \times c_{(HBr,HCl)} \times k_{Obs.}$
0·000	0·1213	0·807	0·353	0·0346
0·0252	0·1467	0·798	0·298	0·0349
0·0402	0·1637	0·793	0·269	0·0349
0·0807	0·2020	0·782	0·216	0·0341
0·1794	0·2907	0·769	0·157	0·0351
0·2540	0·3753	0·763	0·125	0·0346

The constancy of the figures in the last column shows that the rate of reaction is inversely proportional to the active or effective concentration of the hydrogen ion. This is readily explained on the assumption that the ions of formic acid react and not the undissociated molecules. Formic acid is a comparatively weak acid, obeying the dilution law, so that in the presence of excess of hydrogen ion the concentration of formyl ion is inversely proportional to the concentration of the hydrogen ion.

It was anticipated that the influence of the bromine ion on the rate of reaction might be accounted for by the removal of bromine molecules as tribromide ions, provided that these do not take part in the reaction. If the expression (eq. 1) for the equilibrium between free bromine molecules, bromine ions, and tribromide ions is combined with equation 2, which represents the total concentration of bromine in the solution ($= \{Br_2\}$) in terms of the concentration of free bromine molecules ($= [Br_2]$) and of tribromide ions ($= [Br_3']$),

$$\{Br_2\} = [Br_2] + [Br_3'] \quad . \quad . \quad . \quad . \quad . \quad (2)$$

a relation (eq. 3) is obtained between total bromine, free bromine, and bromine-ion concentrations.

$$[Br_2] = \{Br_2\}/[1 + 1/K_1[Br']) \quad . \quad . \quad . \quad . \quad (3)$$

Assuming now that the reaction is due to the free bromine molecules, it is found that the reaction velocity should be proportional to their concentration at any instant, and that the monomolecular velocity coefficient should be related to the bromine-ion concentration by the equation

$$k_{Obs.} = K_2/(1 + 1/K_1[Br']) \quad . \quad . \quad . \quad . \quad (4)$$

Two methods are available for testing these conclusions. The first of these, the results of which are in Table IV, consists in keeping the hydrogen-ion concentration constant by the introduction of a sufficient quantity of hydrobromic acid, which also supplies the minimum excess of bromine ion necessary to give the monomolecular velocity coefficient, and then varying the bromine-ion concentration by the addition of potassium bromide.

TABLE IV.

$c_{HCO_2H} = 0{\cdot}278$ g.-mol. per litre. $c_{HBr} = 0{\cdot}1010N$. $K_1 = 0{\cdot}110$.

c_{KBr} (N).	$c_{(HBr+KBr)}$(N).	$k_{Obs.}$	$k_{Obs.}(1 + 1/K_1[Br'])$.
0·000	0·1010	0·468	0·907
0·050	0·151	0·372	0·908
0·101	0·202	0·316	0·899
0·140	0·251	0·274	0·898
0·202	0·303	0·242	0·883
0·303	0·404	0·194	0·900

The value of the constant K_1 (eqs. 1 and 4) was obtained by plotting the reciprocal of the monomolecular velocity coefficient against the corresponding bromine-ion concentration, and for this it was assumed that all the electrolytes were completely dissociated. A good straight line was obtained (compare eq. 4), and from the point where this cuts the Br′ axis the value of K_1 can be deduced. The constancy of the numbers in the last column shows that for the value of 0·110 for K_1 the figures agree well with the theory, although this is a value considerably higher than that (0·065) found by Jakowkin (*loc. cit.*).

It was realised that a possible reason for the discrepancy may be the assumption made that the electrolytes are completely dissociated; whereas the activity of the bromine ion varies quite considerably over the range of concentration used. Accordingly, in the second method of studying the effect of the bromine ion, a correction has been made for the activity. Here the concentration of the hydrobromic acid was varied and the corresponding monomolecular coefficients were determined. The simple relation that

was shown to exist between the effective concentration of the hydrogen ion and the velocity of the reaction (Table III) was then employed to eliminate the influence of the changing hydrogen-ion concentration.

Table V contains the results of the experiments carried out in order to test this method of attack. The second column gives the activity coefficients for hydrochloric acid (*loc. cit.*) which, as before, were assumed to be not very different from those for hydrobromic acid. The pairs of values of $k_{Obs.}$ given in the fourth column are

TABLE V.

$c_{HCO_2H} = 0{\cdot}278$ g.-mol. per litre. $K_1 = 0{\cdot}070$.
$s = k_{Obs.}\, a \times c_{HBr}\,(1 + 1/a \times k_{Obs.}c_{HBr})$.

c_{HBr} (N).	a.	$a \times c_{HBr}$(N).	$k_{Obs.}$		$a \times k_{Obs.}c_{HBr}$.	s.
0·0555	0·848	0·0471	1·018 1·009	1·014	0·0478	0·0800
0·1110	0·820	0·0911	0·398 0·408	0·398	0·0362	0·0833
0·1665	0·793	0·1320	0·210 0·212	0·211	0·0280	0·0808
0·2220	0·780	0·1730	0·143 0·136	0·140	0·0242	0·0836
0·2775	0·771	0·2140	0·092 0·096	0·094	0·0201	0·0815

the results of pairs of experiments under identical conditions. In the first of each pair, the initial concentration of bromine was about 0·010 g.-mol. per litre, whilst in the second it was about 0·005 g.-mol. per litre. The mean of each pair (fifth column) was used in the subsequent calculations. The activity of the hydrobromic acid is given in the third column. The product of this activity and the corresponding monomolecular velocity coefficient gives (sixth column) the corrected values of $k_{Obs.}$ The reciprocals of these corrected values were plotted against the activities of the hydrobromic acid, or effective concentrations of the bromine ion, and the value of 0·070 for K_1 was deduced from the resulting straight line.* The constancy of the numbers in the seventh column shows that for this value of K_1 the results of the experiments are in good agreement with the theory. It is necessary from the point of view of this treatment that the activity of the tribromide ion should be considered equal to its concentration. This assumption is justified by the fact that the concentration of the tribromide ion is always low. And further, the two experiments of each pair agreed well

* If the value of K_1 is calculated from the results in Table V (as it was in the case of the results in Table IV) without introducing the activities of the ions, the resulting figure is 0·105. This is in good agreement with the value 0·110 obtained from Table IV.

with each other in every case, although the initial concentration of bromine, and therefore of tribromide ion, was halved in the second of the two. For the purpose of accurate comparison with Jakowkin's results (*loc. cit.*) it was necessary to recalculate, using activity coefficients, the value of K_1 from his figures. He gives no results for cases where the concentration of bromine was less than 0·04 g.-mol. per litre, and the value of the constant tends to increase with increasing dilution of the bromine. For this reason, only those figures were considered which refer to the most dilute bromine solutions, and to concentrations of potassium bromide of the same order as those of hydrobromic acid used in the present investigation. The activity coefficients for potassium bromide were taken as identical with those for potassium chloride (Lewis and Randall, *op. cit.*). The mean value of K_1, in terms of the effective concentration or activity of bromine ion, was then calculated to be 0·048 as compared with 0·070, the value deduced from the results in Table V. It follows that, like those in Table IV, the results in Table V agree in giving a figure for K_1 considerably higher than that generally accepted for pure aqueous solutions.

Summary and Discussion.

The reaction between bromine and formic acid has been studied in dilute aqueous solution, using the Ostwald isolation method. It is shown that formic acid is completely oxidised to carbon dioxide. The reaction is of the second order, but the rate is retarded by the hydrobromic acid produced. From a study of the separate effects of the hydrogen and bromine ions, it is deduced that the reaction takes place between the formyl ions and free bromine molecules, *i.e.*, those molecules of bromine which are not combined with bromine ions to give the complex ions Br_3'. It is necessary to give to the constant for the equilibrium between bromine molecules, bromine ions, and tribromide ions a value considerably higher than that due to Jakowkin. Jakowkin's experiments, however, were performed with concentrations of bromine considerably higher than those used in the present investigation, and his constants show a regular increase with increasing dilution of bromine.

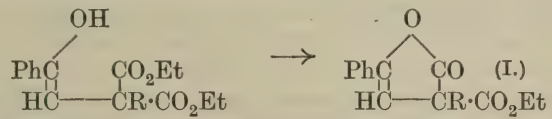
THE BALLIOL AND TRINITY LABORATORIES,
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CCCLXXII.—*Lactonic Esters derived from Phenacyl Bromide by Condensation with Ethyl Sodiomalonate and Analogous Substances.*

By Ramoni Mohan Rây and Jñanendra Nath Rây.

The primary object of this work, *viz.*, the preparation of *ac*-substituted tetrahydronaphthalenes, was not achieved.

o-Benzoylbenzoic acid is readily convertible into anthraquinone. It was hoped, therefore, that phenacylmalonic ester under suitable conditions would pass into a tetrahydronaphthalene derivative. In presence of 6% aqueous potassium hydroxide, however, the reaction followed another course, the *lactone* I (R=H) being formed, which gave benzoic acid on oxidation.



(R=H, Me, Et, COMe, CH_2Ph, or $CHMe_2$.)

Lactones of type I were also formed in the reactions between phenacyl bromide and the sodio-derivatives of malonic, benzylmalonic, *iso*propylmalonic, acetylmalonic, and benzoylmalonic esters. Varying quantities of acetophenone also were produced, due to reduction of phenacyl bromide.

Phenacyl bromide, ethyl cyanoacetate, and sodium ethoxide reacting in molecular quantities in alcoholic solution gave *ethyl diphenacylcyanoacetate*, $(COPh\cdot CH_2)_2C(CN)\cdot CO_2Et$, but when dry ethyl sodiocyanoacetate (2 mols.) was heated for several hours with phenacyl bromide (1 mol.) suspended in dry benzene, a substance, m. p. 125—127°, was obtained which is believed to be the mono-substitution product. This could not be converted into a tetrahydronaphthalene derivative under a variety of conditions.

Experimental.

The reactions of phenacyl bromide with the following substances were examined.

With Ethyl Sodiomalonate.—The sodio-derivative (prepared from 0·7 g. of sodium and 5 c.c. of ethyl malonate) in cooled absolute alcohol (30 c.c.) was shaken vigorously with phenacyl bromide (6 g.). After 10 minutes, the mixture, now neutral, was poured into much water; by extraction with ether, ethyl phenacylmalonate was obtained as an oil (8 g.), *d* 1·2.

The crude ester was shaken in the cold with 6% potassium

hydroxide solution (65 c.c.). The red, semi-solid mass that had separated after 12 hours was crystallised from rectified spirit, the *lactone* (I; R=H) of α-carbethoxy-γ-hydroxy-γ-phenyl-Δ^{β}-propenecarboxylic acid being obtained in colourless needles, m. p. 105° (Found: C, 67·6. $C_{13}H_{12}O_6$ requires C, 67·2%).*

By keeping the lactone (1 g.) for 12 hours in a minimum of cold alcohol saturated with dry ammonia, the corresponding *amide*, $C_{10}H_7O_2{\cdot}CO{\cdot}NH_2$, was obtained in long needles, m. p. 153—154° after crystallisation from dilute alcohol (Found: N, 7·1. $C_{11}H_9O_3N$ requires N, 6·9%).

The lactone (1 g.) was oxidised with *N*/10-sulphuric acid (50 c.c.) and *N*/10-potassium permanganate (excess) on the boiling-water bath. Ether extracted benzoic acid from the product after the usual treatment.

With Ethyl Sodiocyanoacetate.—An alcoholic solution of the reactants (1 mol. of each) was heated on the water-bath for ½ hour and then poured into water. The precipitate formed was removed after 12 hours; the filtrate gave nothing to ether. By fractionally crystallising the precipitate from 50% alcohol, *ethyl diphenacylcyanoacetate*, m. p. 141° (Found: N, 4·3. $C_{21}H_{19}O_4N$ requires N, 4·0%), was obtained together with a small quantity of a substance, m. p. 125—127°.

With Ethyl Acetylsodiomalonate.—Ethyl acetylmalonate was prepared by treating "molecular" sodium (1 atom.) with ethyl malonate in ice-cold, dry ether and warming the mixture with acetyl chloride (1·25 mols.) at 33° for an hour. The product after decomposition with a small quantity of water was shaken with ether. The dried extract was fractionated; the portion, b. p. 125—128°/17 mm., was pure acetylmalonate (yield 60%).

Ethyl acetylmalonate (4 c.c.) was added to alcoholic sodium ethoxide (0·46 g. of sodium in 25 c.c.); the mixture was treated with 4 g. of phenacyl bromide and, after a few minutes, warmed at 50—55° for ¼ hour. Ether extracted from the product, diluted with water, the *lactone* (I; R=CO·CH_3) of ethyl α-acetyl-γ-hydroxy-γ-phenyl-Δ^{β}-propenecarboxylic acid, which crystallised from alcohol and ether in needles, m. p. 135—136° (Found: C, 65·6. $C_{15}H_{14}O_5$ requires C, 65·7%).

As ethyl acetylmalonate is easily decomposed into ethyl acetoacetate by alkali, the compound, m. p. 119—120°, prepared from phenacyl bromide and ethyl sodioacetoacetate was compared with the preceding lactone; it depressed its m. p.

With Ethyl Sodioethylmalonate.—The reaction was carried out as

* The humidity of the air (*ca.* 80%) made determinations of hydrogen almost impossible.

in the case of ethyl sodiomalonate. The *lactone* produced (I; R=Et) crystallised from alcohol in needles, m. p. 134—135° (Found: C, 69·3. $C_{15}H_{16}O_4$ requires C, 69·2%).

With Ethyl Sodiobenzylmalonate.—The *lactone* (I; R=CH_2Ph) obtained crystallised from alcohol in flat needles, m. p. 125° (Found: C, 73·8; H, 6·2. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6%).

With Ethyl Sodioisopropylmalonate.—The constituents in molecular proportions were boiled in alcoholic solution on the water-bath for 1 hour. The product, on dilution with water, deposited the *lactone* (I; R=$CHMe_2$), which crystallised from alcohol in needles, m. p. 151° (Found: C, 69·7; H, 6·5. $C_{16}H_{18}O_4$ requires C, 70·1; H, 6·5%).

Our thanks are due to Sir P. C. Rây for his interest in this work.

College of Science, Calcutta. [*Received, September 3rd*, 1925.]

CCCLXXIII.—*Equilibrium in the System:* $CH_3{\cdot}CO{\cdot}O{\cdot}CH_3 + H_2O \rightleftharpoons CH_3{\cdot}OH + CH_3{\cdot}CO{\cdot}OH$.

By George Joseph Burrows.

From the results of experiments on the rate of hydrolysis of methyl acetate by acids in the presence of various amounts of water and acetone it appeared that the equilibrium between the ester, water, alcohol, and acetic acid varied considerably. Jones and Lapworth (J., 1911, **99**, 1427) have shown that the equilibrium constant of ethyl acetate varied between 6 and 9 for solutions containing hydrochloric acid, in which the ratio of molecules of water to hydrogen chloride varied from 6·2 to 4·6. In the case of methyl acetate, Berthelot and Péan de St. Gilles (*Ann. Chim. Phys.*, 1863, **68**, 225) found that if equivalent quantities of acetic acid and methyl alcohol were mixed, 67·5% of each had combined at equilibrium, from which result $K = 4{\cdot}31$. The value obtained from Menschutkin's results (*Annalen*, 1879, **195**, 334) is $K = 5{\cdot}18$, whilst Worley (*Proc. Roy. Soc.*, 1912, *A*, **87**, 582) deduced the value 6·6 by extrapolation for a solution containing no added catalyst.

Results are now given for the value of K for solutions containing relatively low concentrations of water, and the effect of diluting the system with various quantities of water, methyl alcohol, and acetone has been studied. The acetone was added with the intention of diluting the system with a substance not participating in the reaction. Special precautions were taken to dehydrate the alcohol, ester, and acetone. It has been found that the value of K is dependent not

only on the ratio $[H_2O]:[HCl]$, but also on the amount of methyl alcohol or acetone present in the solution. Only for solutions containing a large excess of methyl alcohol is K in the neighbourhood of 4 : in all other cases it is considerably greater. For solutions containing approximately equal amounts of water and ester, in which the ratio of molecules of water to hydrogen chloride is not greater than 7 to 1, K is greater than 12. As the amount of water relative to hydrogen chloride is increased, the equilibrium constant decreases, approaching 7 as the limiting value for a solution in which the ratio $[H_2O]:[HCl]$ is about 1000. The value of K is also decreased by the addition of acetone to the solution, the effect being smaller than that observed when the system is diluted with excess of water.

A considerably greater effect is observed when the system contains a large excess of methyl alcohol. Thus for a solution in which the ratio [HCl] to $[H_2O]$ to $[CH_3{\cdot}OH]$ was 1 to 7·8 to 2·2, K was 11·92, whereas the values 5·87 and 4·34, respectively, were obtained for solutions in which the ratios were 1 to 9·6 to 32·6 and 1 to 625 to 2639.

This displacement of the equilibrium by hydrogen chloride indicates that the latter alters the activity of one or more of the reactants so that the total concentrations of water, methyl acetate, acetic acid and methyl alcohol found at equilibrium in the usual way are in reality not the concentrations actually participating in the equilibrium. At present it is not possible to state what fraction of each of the substances is rendered inactive in this way, but the results recorded here are capable of explanation by such a theory. It is now definitely established that in a solution of hydrogen chloride in water, only a portion of the hydrogen chloride and water molecules are in an active condition. Thus from electromotive-force or vapour-pressure measurements of a series of such mixtures one can calculate the activity of water in the presence of different amounts of hydrogen chloride. The figures in the seventh column in Table I, taken from the results of Dobson and Masson (J., 1924, **125**, 671), represent the fraction of the water molecules in each particular solution that are in the active condition. The figures in the eighth column are obtained by multiplying K by the " water activity " in each case, and it will be seen that these numbers are constant and equal to about 7. This would indicate that the concentration of water participating in the equilibrium is the same as the active concentration found from vapour-pressure measurements. Furthermore, the constancy of this product points to the fact that, for the particular concentrations in this series, the effect of the hydrogen chloride on the equilibrium constant is due almost entirely

to its effect on the activity of the water. There can be no doubt that the catalyst affects to some extent the activity of the other reactants, but it would appear from these results that this effect is negligible in comparison with the effect on the water, or else the individual effects on the ester, alcohol, and acetic acid neutralise one another or have a constant value in these cases.

Figures are not available for the effect of hydrogen chloride on the activity of these three substances. McBain and Kam (J., 1919, **115**, 1332) have recorded results for the vapour pressures of mixtures of water and acetic acid at the boiling point, with and without the addition of neutral salts. These authors concluded from their results that "many salts enhance the partial vapour pressure of acetic acid in aqueous solution by very appreciable amounts. The undissociated acid must be regarded as exhibiting enhanced chemical potential in the presence of such salts." The increase in the partial pressure is proportional to the concentration.

The results given in Tables VI and VII can be explained, at least qualitatively, on the assumption that the addition of hydrogen chloride to an aqueous solution of acetic acid has an effect on the activity of the molecules of the latter similar to that resulting from the addition of a neutral salt. The addition of a large excess of methyl alcohol to the system under discussion results in a marked decrease in the value of K. But an increase in the concentration of methyl alcohol relative to hydrogen chloride corresponds to a decrease in the concentration of acetic acid relative to hydrogen chloride, *i.e.*, to an increase in hydrogen chloride relative to acetic acid. The observed decrease in K with increasing alcohol concentration can thus be explained on the assumption that it results from an increase in the activity of the acetic acid under these conditions. At present it is not possible to treat the subject quantitatively, but experiments are now in progress from which it is hoped to determine the actual effect of hydrogen chloride on each of the reactants in a system such as this.

Experimental.

Freshly distilled methyl acetate mixed with the desired quantity of water and hydrochloric acid was kept for 2 or 3 days in a stoppered flask, until the mixture had become homogeneous. The weight of hydrogen chloride in a given weight of the acid used was previously determined. Small quantities of this stock solution were then mixed with various amounts of water, acetone, methyl alcohol, or methyl acetate, and sealed in hard glass tubes which had previously been steamed and dried. All quantities of the different liquids were weighed. The liquids used were purified and dehydrated by suitable means and their purity was ascertained by boiling point

and density determinations. The acetone and methyl alcohol were dehydrated with metallic calcium. The methyl acetate was freed from acid by means of sodium carbonate and dehydrated with calcium chloride. It was then distilled, the middle portion of the distillate being used in these experiments. A sample treated in this way was hydrolysed with barium hydroxide solution, and the amount of methyl acetate found was 99·7% of the theoretical.

The tubes containing the different solutions were kept in a thermostat at 25·0° for different intervals of time, varying from 2 to 10 weeks, according to the amount of hydrochloric acid present. The tubes were then opened under neutral sodium acetate solution, and the amount of acetic acid was determined by titration with barium hydroxide solution. Blank experiments were performed which showed that the solutions had no determinable effect on the glass tubes.

The figures given in the following tables represent the number of gram-molecules of the different substances present at equilibrium. The values of the equilibrium constant were calculated from the equation $K = [AcOMe][H_2O]/[AcOH][MeOH]$.

The effect of hydrogen chloride on the equilibrium constant is shown by the results in Table I. For the first four experiments, in which the amount of water was comparatively small, K is much larger than is the case for the solutions for which the ratio $[H_2O] : [HCl]$ was high. As stated above, the products of these high values of K and the " water activity " are approximately constant.

TABLE I.

$[HCl] \times 10^3$.	$[AcOMe] \times 10^3$.	$[H_2O] \times 10^3$.	$\frac{[AcOH]=[MeOH]}{\times 10^3}$.	$\frac{[H_2O]}{[HCl]}$.	K.	Water activity, a.	Ka.
5·57	84·86	31·14	14·36	6·82	12·82	0·525	6·8
4·245	44·57	31·84	10·80	7·50	12·17	0·56	6·8
4·49	34·10	34·74	9·935	7·74	12·01	0·57	6·8
4·59	34·00	35·96	10·13	7·83	11·92	0·58	6·9
4·53	24·81	135·7	19·65	30·0	8·72		
5·01	2·76	261·6	9·565	52·2	7·89		
0·446	32·44	36·8	12·33	82·5	7·85	*	
0·444	25·14	113·6	19·40	255·9	7·59		
0·0576	19·65	27·80	8·667	482·7	7·27		

* Accurate figures for the value of the " water activity " in dilute solutions are not available, but by interpolation from the other values the activity in these five cases is found to vary from about 0·9 to 1. The product $K \times$ " water activity " for these dilute solutions is therefore approximately 7.

In the next series of experiments the effect of diluting the system with acetone was studied. The results are in Tables II, III, and IV.

TABLE II.

[HCl] $\times 10^3$.	[AcOMe] $\times 10^3$.	[H_2O] $\times 10^3$.	[AcOH]=[MeOH] $\times 10^3$.	[Me_2CO] $\times 10^3$.	K.
4·49	34·10	34·74	9·935	—	12·01
4·53	34·34	35·00	10·17	8·00	11·63
4·48	33·78	34·44	10·14	21·1	11·32
4·48	33·64	34·30	10·31	53·7	10·85
4·49	33·61	34·27	10·43	79·7	10·60
1·34	9·85	10·05	3·147	106·0	9·99

The ratio [H_2O] : [HCl] is nearly constant throughout the above series and is equal to 7·7.

TABLE III.

[HCl] $\times 10^3$.	[AcOMe] $\times 10^3$.	[H_2O] $\times 10^3$.	[AcOH]=[MeOH] $\times 10^3$.	[Me_2CO] $\times 10^3$.	K.
4·59	34·00	35·96	10·13	—	11·92
4·59	33·86	35·83	10·32	14·3	11·4
4·54	33·25	35·18	10·43	30·0	10·75
4·49	32·81	34·74	10·38	53·4	10·58

Although the results in these two tables are very similar, they represent two distinct sets of experiments, the solutions being prepared from entirely different samples.

TABLE IV.

[HCl] $\times 10^3$.	[AcOMe] $\times 10^3$.	[H_2O] $\times 10^3$.	[AcOH]=[MeOH] $\times 10^3$.	[Me_2CO] $\times 10^3$.	K.
0·446	32·44	36·80	12·33	—	7·85
0·444	32·21	36·57	12·33	8·26	7·75
0·391	28·28	32·12	10·91	2·52	7·63
0·446	32·12	36·47	12·64	16·0	7·33
0·446	32·02	36·40	12·75	29·2	7·17
0·444	31·82	36·18	12·79	38·8	7·04
0·445	31·82	36·19	12·83	47·2	7·00

The ratio [H_2O] : [HCl] in this case is 81.

The results in these three tables show that the presence of acetone decreases the value of the equilibrium constant, but when the ratio [H_2O] : [HCl] is low the effect is less than that caused by the addition of the same number of molecules of water to the system (Tables II and III), whereas it is apparently greater in the case of a solution in which there is a great excess of water over hydrogen chloride (Table IV). In the former case, a solution containing 7·7 molecules of water and 79 of acetone to 1 of hydrogen chloride gives a value for K equal to 10, whereas a solution containing 86 molecules of water to 1 molecule of the acid would have a value of 7·8. In the latter case, however, the value for a solution containing 80 molecules of water and 106 of acetone to 1 of hydrogen chloride is less than that for a solution containing 186 molecules of water.

The effect of increasing the concentration of methyl acetate is shown by the results in Table V; K increases slightly with increasing concentration of ester.

TABLE V.

[HCl] × 10^3.	[AcOMe] × 10^3.	[H_2O] × 10^3.	[AcOH]=[MeOH] × 10^3.	K.
4·59	34·00	35·96	10·13	11·92
4·25	44·57	31·84	10·80	12·17
4·64	64·61	33·42	13·22	12·36
4·56	79·88	31·61	14·08	12·74

The effect of adding methyl alcohol to the system is shown by the results in Tables VI and VII.

TABLE VI.

[HCl] × 10^3.	[AcOMe] × 10^3.	[H_2O] × 10^3.	[MeOH] × 10^3.	[AcOH] × 10^3.	[MeOH] : [HCl].	K.
4·59	34·00	35·96	10·13	19·13	2·2	11·92
4·57	38·45	40·37	33·57	5·51	7·3	8·39
4·59	40·34	42·30	63·16	3·794	13·8	7·12
4·60	42·13	44·08	149·4	2·118	32·6	5·87

In this series the ratio [H_2O] : [HCl] increases from 7·7 to 9·6.

TABLE VII.

[HCl] × 10^3.	[AcOMe] × 10^3.	[H_2O] × 10^3.	[MeOH] × 10^3.	[AcOH] × 10^3.	[MeOH] : [HCl].	K.
0·0576	19·65	27·80	8·667	8·667	150·5	7·27
0·0576	26·03	34·22	79·20	2·418	1375	4·65
0·0576	27·63	36·02	152·0	1·51	2639	4·34

In this series the ratio [H_2O] : [HCl] increases from 483 to 625.

The usually accepted value for the equilibrium constant was found only in the last two experiments of this particular series. It is concluded, from the results given in the last column of Table I, that the true equilibrium constant corrected for the effect of hydrogen chloride is 7, and that the low results given in Table VII are due to the effect of the hydrogen chloride on the acetic acid, just as the high values of K in Table I are attributable to its effect on the activity of the water.

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THE UNIVERSITY, SYDNEY. [*Received, September 16th,* 1925.]

CCCLXXIV.—*Synthesis of* 2 : 3 : 5 *(or* 2 : 3 : 4)-*Trimethyl Glucose.**

By JAMES COLQUHOUN IRVINE and JOHN WALTER HYDE OLDHAM.

RECENT developments in the constitutional study of carbohydrates demand that, from time to time, the structure of the simple methylated sugars utilised as reference compounds in such work should be brought under review. In the present case, we have selected 2 : 3 : 5-trimethyl glucose for further examination, as this sugar is the key to the constitution of both maltose and β-glucosan, and acquires further importance in connexion with the chemistry of starches. Obviously the significant feature of this particular form of trimethyl glucose is the non-reducing hydroxyl group, as the identification of its position indicates the linkage of the two glucose residues in maltose and also the attachment of the anhydro-ring in β-glucosan. In order to give a clear view of the present position, it may be recalled that 2 : 3 : 5-trimethyl glucose was first obtained, in the form of the corresponding methylglucoside (Purdie and Irvine, J., 1903, **83**, 1021; Purdie and Bridgett, *ibid.*, 1037) by methylating methylglucoside in the presence of excess of methyl alcohol. The free sugar was also studied by the above workers, who converted it into 2 : 3 : 5 : 6-tetramethyl glucose and tentatively ascribed to it the structure still in use. Their views were afterwards supported by Irvine and Dick (J., 1919, **115**, 593), who showed that, on oxidation by nitric acid, the sugar is converted into a trimethyl saccharo-lactone. This observation was confirmed by Haworth and Leitch (*ibid.*, 809), who isolated the same sugar from fully methylated maltose, and by Irvine and Oldham (J., 1921, **119**, 1744) in studying the structure of β-glucosan. Although there seemed no reasonable doubt that the methylated glucose in question was correctly formulated, the evidence obtained by subjecting sugars to the oxidising action of nitric acid should not be accepted as final so long as other and more diagnostic tests are available. The divergent results obtained by Irvine and Hogg (J., 1914, **105**, 1386) and by Levene and Meyer (*J. Biol. Chem.*, 1922, **54**, 805) in oxidising monomethyl glucose by means of nitric acid may be quoted in illustration of this point.

The constitution of 2 : 3 : 5-trimethyl glucose has now been

* In a letter to *Nature*, 19th September, 1925, Haworth states that he has obtained evidence leading to the conclusion that normally the oxidic ring in glucose couples positions 1 and 5. Should this be substantiated, the methylated glucose which forms the subject of the present communication should be indexed as 2 : 3 : 4-trimethyl glucose.

confirmed by the following synthetical scheme, which was designed to produce a methylated glucose with unsubstituted hydroxyl groups definitely in the terminal positions 1 and 6.

Stage I. Triacetyl glucosan was converted by Karrer's process into triacetyl dibromoglucose, identical with that previously obtained by Fischer from penta-acetyl glucose.

Stage II. The above dibromo-derivative, when treated with methyl alcohol in the presence of silver carbonate, gave triacetyl methylglucoside bromohydrin, and the subsequent reactions were therefore designed to replace acetyl by methoxyl and thereafter to introduce the hydroxyl group in place of bromine.

Stage III. The acetyl groups were removed by the action of alcoholic ammonia, giving methylglucoside bromohydrin. It may be mentioned that, although the physical constants were otherwise in good agreement, the melting point of this compound was found to be several degrees higher than that quoted by Fischer.

Stage IV. Methylation of methylglucoside bromohydrin under conditions which would have the minimum effect on the bromine atom was achieved by the silver oxide reaction and gave a mixture of (*a*) trimethyl methylglucoside bromohydrin (80%) and (*b*) the corresponding enolic anhydride (20%). From this mixture, pure trimethyl methylglucoside bromohydrin was isolated.

Stage V. The above compound, when heated at 150° with alcoholic potassium acetate, gave a 72% yield of pure crystalline trimethyl β-methylglucoside identical with that obtainable from the form of trimethyl glucose which is the subject of the investigation. This result supplies the evidence required.

In the glucoside finally obtained, the hydroxyl group occupies the position of the bromine atom in triacetyl methylglucoside bromohydrin. As Fischer succeeded in reducing the latter to triacetyl methyl*iso*rhamnoside (*Ber.*, 1912, **45**, 3761), the group is therefore in the 6-position. In consequence, the methyl groups in the corresponding sugar must be in positions 2, 3, and 5. Although we are unwilling to attach undue importance to colour tests, the proof is strengthened by the following considerations. In the glucose molecule positions 1, 2, 3, and 5 are occupied by secondary alcohol groups, and the only primary alcohol group is in the 6-position. If, therefore, the vacant hydroxyl group in a trimethyl methylglucoside is primary, the corresponding nitro-derivative should give a red colour by Meyer's test; otherwise a blue solution will result. Trimethyl methylglucoside bromohydrin was therefore converted into the corresponding iodohydrin, which was transformed with some difficulty into mononitro-trimethyl methylglucoside. This, on treatment with nitrous acid, gave, as

expected, the characteristic red colour similar to that obtained from nitromethane.

In verification of our former work on β-glucosan we have repeated the conversion of this anhydroglucose into trimethyl glucose and subjected the sugar to the following successive operations :

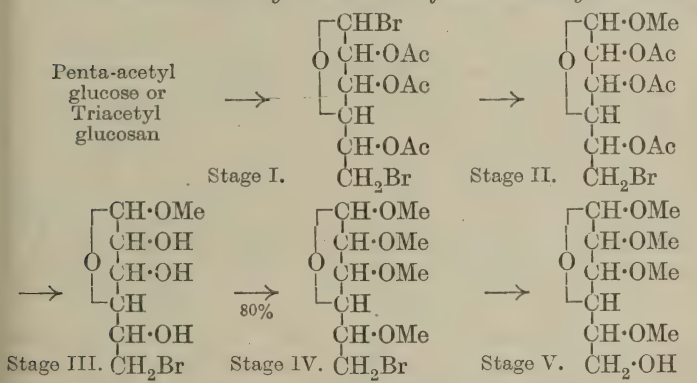
I. Acetylation, giving trimethyl glucose diacetate.

II. Bromination, by the action of hydrogen bromide in glacial acetic acid, giving trimethyl acetyl glucose bromohydrin.

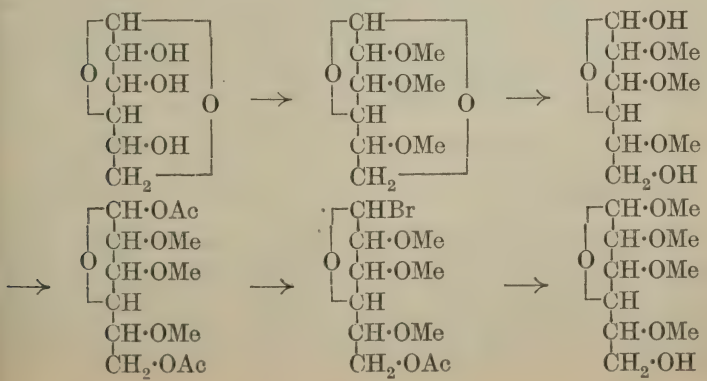
III. Action of sodium methoxide, giving trimethyl β-methyl-glucoside.

The methylated glucoside finally isolated was identical with that obtained in the synthetical processes already synopsised, thus confirming that β-glucosan is 1 : 6-anhydroglucose. In order to render the scheme of reactions intelligible the various changes involved in the two alternative methods of producing 2 : 3 : 5-trimethyl methylglucoside may be represented structurally :

I. *From Penta-acetyl Glucose or from Triacetyl Glucosan.*



II. *From Glucosan.*



The collective results may be compressed into the statement that dibromotriacetyl glucose, maltose, and glucosan are all convertible into the same form of trimethyl glucose.

We are engaged in attempts to synthesise other partly methylated sugars and, the isomeric distinction between 2 : 3 : 5- and 2 : 3 : 6-trimethyl glucose having now been established, the results will be utilised in forthcoming papers from this laboratory.

Experimental.

The following account of experimental procedure is limited to the synthetical reactions described in the introduction. Other reactions to which reference is made were carried out by methods which are now standardised, and their description is therefore omitted.

Triacetyl Dibromoglucose from Triacetyl β*-Glucosan.*—The method recommended by Karrer (*Helv. Chim. Acta*, 1922, **5**, 124) was adopted, minor variations being introduced, as the reaction, which is most successful when small quantities of material are manipulated, requires careful control. Triacetyl β-glucosan (in lots of 5 g.) was heated on a boiling water-bath with phosphorus pentabromide (8·5 g.), the flask being fitted with a ground-in condenser. When effervescence had nearly ceased, the contents were poured into finely-crushed ice and thoroughly disintegrated by a glass rod. Similarly, the residue in the flask was mixed as rapidly as possible with small pieces of ice until all halides of phosphorus had been destroyed. Rise of temperature must be avoided in these operations.

The fine white powder resulting from several experiments was united, washed with water until free from phosphoric acid, and thereafter with absolute alcohol until the washings were nearly colourless. Purification was effected by dissolving in a small quantity of chloroform and precipitating with light petroleum. The yield of crystalline product (m. p. 173°), including the material obtained from the mother-liquors, averaged 50% of the theoretical amount. As the rotation of the compound does not appear in the literature, the following values were determined:

Solvent.	*c.*	$[\alpha]_D$.
Chloroform	1·537	+189·9°
Glacial acetic acid	1·256	+185·9

Conversion of Triacetyl Dibromoglucose into Triacetyl Methylglucoside Bromohydrin.—This reaction was carried out exactly as described by Fischer (*Ber.*, 1902, **35**, 857; 1920, **53**, 873), the yield of glucoside being nearly quantitative; after recrystallisation from absolute alcohol, the product melted at 126—127°. As in

this case also no optical data appear to have been published, the specific rotation in the following solvents was determined :

Solvent.	c.	$[\alpha]_D$.
Chloroform	3·012	−1·4°
Methyl alcohol	3·014	−3·1
Glacial acetic acid	3·006	−2·7

Methylglucoside Bromohydrin.—The acetylated methylglucoside bromohydrin obtained as above was dissolved at room temperature in methyl alcohol containing 5—10% of ammonia so as to form a 5% solution. It is unnecessary to saturate the liquid with ammonia as stated by Fischer and the use of a dilute solution enables the end-point of the reaction to be determined polarimetrically. When the specific rotation had diminished to − 19·3°, the product was isolated by evaporating to dryness and extracting with chloroform to remove acetamide. The yield of crude bromohydrin was nearly quantitative, and after recrystallisation from ethyl acetate, the compound melted and decomposed at 153—154° in place of 148° as quoted by Fischer. In aqueous solution, under conditions identical with those used by Fischer, the specific rotation was − 33·6°, the literature value being − 34·9°.

Tribenzoyl methylglucoside bromohydrin has no direct bearing on the main investigation, but reference may be made to it. The normal procedure was followed, the bromohydrin being acted on by a slight excess of benzoyl chloride dissolved in pyridine. The product was brought into solution in a minimum of glacial acetic acid, and the pure tribenzoate precipitated by addition of absolute alcohol : m. p. 160—162°; $[\alpha]_D$ in chloroform − 5·0° for $c = 2·413$; needles, insoluble in water and light petroleum, and readily soluble in organic solvents with the exception of alcohol and ether.

Trimethyl Methylglucoside Bromohydrin.—For the particular object in view, alkylation by silver oxide and methyl iodide is the only method applicable to methylglucoside bromohydrin. The usual procedure was followed, methyl alcohol being added during the first methylation. After four successive treatments, the refractive index was constant and the liquid product was distilled, a mobile syrup being obtained (b. p. 140°/1 mm.; n_D 1·4720; $[\alpha]_D$ in methyl alcohol − 20·5° for $c = 1$). Examination showed that at least two compounds were present, one of them containing no bromine. This constituent was present to the extent of 20% and was evidently dimethyl anhydromethylglucoside (Found : C, 42·7; H, 6·7; OMe, 41·7; Br, 21·3. Calc. for trimethyl methylglucoside bromohydrin, C, 40·1; H, 6·35; OMe, 41·4; Br, 26·7%. Calc. for a mixture of 80% of the above with 20% of trimethyl anhydromethylglucoside, C, 42·7; H, 6·6; OMe, 42·2; Br, 21·3%).

The close agreement with the experimental figures, particularly the result of bromine determinations, confirms the composition ascribed to the mixture. The constituents were separated by solution in ether and repeated extraction with water, a process which completely removed dimethyl anhydromethylglucoside. After evaporation of the ether the residual syrup was fractionated in a high vacuum, giving a liquid distillate which slowly crystallised. Owing to the ready solubility of the compound in all solvents with the exception of water, no suitable recrystallising medium could be found but, after spreading on a tile, the crystals were hard and crisp : m. p. 24° ; n_D 1·4735 ; $[\alpha]_D$ in acetone — 5·8° (c = 3·851), in methyl alcohol — 4·7°, in benzene — 7·7°, in chloroform — 3·5° (Found : C, 40·3; H, 6·3; OMe, 41·3; Br, 27·2. Trimethyl methylglucoside bromohydrin requires C, 40·1; H, 6·35; OMe, 41·4; Br, 26·7%).

Hydroxylation of Trimethyl Methylglucoside Bromohydrin.—Preliminary experiments having shown that both aqueous and alcoholic sodium hydroxide react with the bromohydrin, eliminating hydrogen bromide and giving unsaturated derivatives, the hydroxylation was effected by means of potassium acetate. A 3% solution of the bromohydrin in methyl alcohol was heated with excess of potassium acetate at 150° for 3 days, during which the lævorotation increased greatly. The crude product, on isolation in the usual manner, was obtained in nearly quantitative amount but was contaminated with an unsaturated impurity. On keeping, however, the syrup solidified and, after draining on a tile and recrystallising from light petroleum, a 72% yield of pure trimethyl β-methylglucoside was obtained in characteristic crystals. The melting point was 93—94°, a value which was unaffected when the material was mixed with an authentic specimen of the compound. The specific rotation also was in close agreement ($[\alpha]_D$ in chloroform — 11·9° for c = 1·084). It was ascertained that owing to the alkalinity of potassium acetate the above hydroxylation was accompanied by a side-reaction giving rise to an unsaturated compound; this is being further examined.

Trimethyl Methylglucoside Iodohydrin.—The general method described by Finkelstein (*Ber.*, 1910, **43**, 1528) was employed, a solution of trimethyl methylglucoside bromohydrin in acetone being heated at 100° for 6 hours with twice the theoretical amount of sodium iodide. After removal of the acetone, the residue was extracted several times with ether and the united extracts were washed with aqueous sodium thiosulphate solution, allowed to stand over sodium sulphate, and evaporated to dryness. The product crystallised readily in needles and, when drained on a tile,

melted at 31—34°. Owing to the excessive solubility in all solvents except water, no recrystallising medium could be found, but the compound was evidently pure (Found: OMe, 36·1; I, 36·5. Calc., OMe, 35·8; I, 36·7%; n_D 1·4992; $[\alpha]_D$ + 8·6° in chloroform for $c = 3·637$, + 4·1° in acetone for $c = 3·897$, and + 6·5° in methyl alcohol for $c = 4·221$).

Trimethyl methylglucoside iodohydrin was converted into the corresponding nitro-compound by heating with dry silver nitrite at 100° for 2 days. After distillation under diminished pressure the nitro-derivative was isolated in the form of the sodium salt by the addition of the calculated amount of sodium methoxide dissolved in methyl alcohol. On removal of the solvent, the salt was dissolved in dilute sulphuric acid, and the solution extracted with ether. After being washed with sodium thiosulphate solution to remove a trace of iodine, the ethereal layer was dried and evaporated, and the mononitro-trimethylglucoside isolated by distillation as a colourless syrup (n_D 1·4603). Beyond checking the methoxyl content (Found: OMe, 46·4. Calc., OMe, 46·7%), the compound was not fully analysed, as it was prepared solely for the purpose of carrying out the colour test with sodium nitrite and dilute sulphuric acid. This treatment gave a bright red solution, free from any shade of blue and, whilst the colour was not so intense or so lasting as that obtained under parallel conditions with nitromethane, the result was characteristically positive.

The thanks of the authors are due to the Carnegie Trust for a Fellowship which has enabled one of them to take part in the work.

United College of St. Salvator and St. Leonard,
University of St. Andrews. [*Received, October 7th,* 1925.]

CCCLXXV.—*Glycerol Glucoside.*

By Helen Simpson Gilchrist and Clifford Burrough Purves.

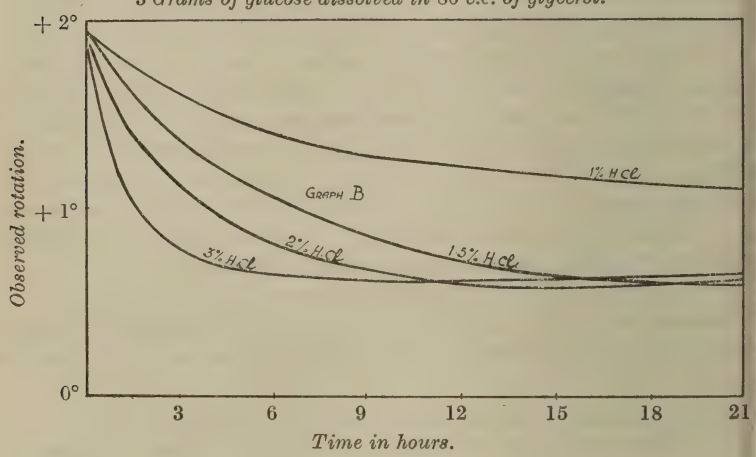
Few condensation reactions between reducing sugars and polyhydric compounds of simple type have been studied, possibly owing to the difficulty of producing such compounds and of purifying them when formed. As, in the case of glucose and glycerol, condensation leads to a type of compound which may be regarded as analogous to a carbohydrate fat and is of physiological interest, we have taken up the investigation of this subject.

Glycerol glucoside, which was originally described by Fischer (*Ber.*, 1894, **27**, 2483), has now been obtained on the large scale

by an improved process. The older method, involving as it does the saturation of a glycerol solution of glucose with hydrogen chloride, is tedious, but the same compound is more readily obtained by limiting the acid concentration to 0·25% and heating at 100°. The product in each case is a syrup possessing the properties of a glucoside, but no information bearing on the composition or structure of the compound has hitherto been available, and it was unknown to which type the glucose residue belongs or to which part of the glycerol molecule it is attached. These questions have been solved by methylation, which yielded *hexamethyl glycerol glucoside* as a colourless, volatile liquid, b. p. 190—192°/12 mm. Hydrolysis thereafter yielded 2 : 3 : 5 : 6-tetramethyl glucose

FIG. 1.

3 Grams of glucose dissolved in 80 c.c. of glycerol.



together with a dimethyl glycerol which was shown to be αβ-dimethoxy-γ-hydroxypropane. From these results, the constitution of the parent glucoside is established to be:

$$CH_2(OH)\cdot CH(OH)\cdot CH\cdot CH(OH)\cdot CH(OH)\cdot CH\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$$
$$\text{└——————O——————┘}$$

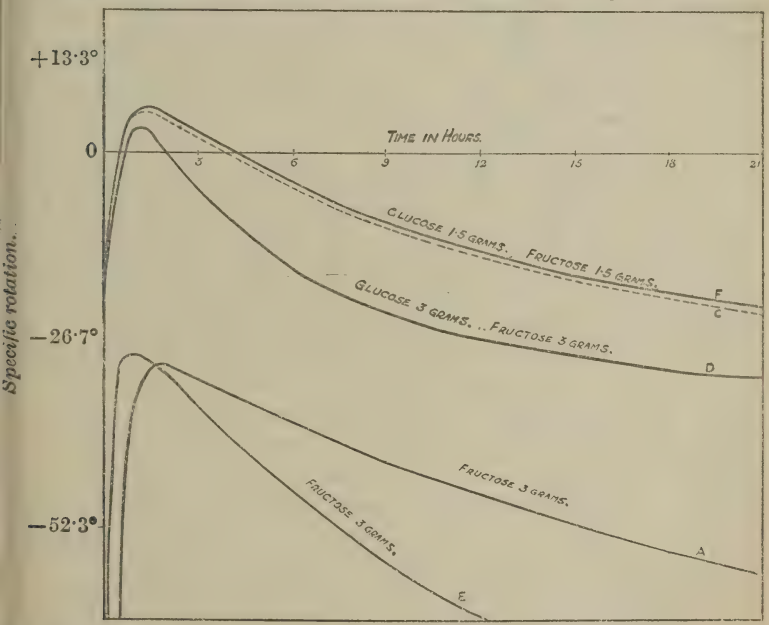
The compound, as prepared, is a mixture of α- and β-forms and the optical values determined on hydrolysing the methylated derivatives show that glycerol γ-glucosides were present only in small amount, the limits in different preparations being 1·95 and 0·93%. The research was accordingly extended by varying the conditions of condensation, the changes in rotation which take place when glucose is dissolved in glycerol containing hydrogen chloride being utilised to study the reaction. The concentration o

the sugar in no case exceeded 6% by weight of the glycerol employed and solutions containing more than 3% by weight of the acid were not examined. These limitations were found to be necessary, as, when exceeded, the high viscosity or the depth of colour resulting made polarimetric observations uncertain. For the same reason the experiments were carried out at room temperature.

In Fig. 1 the rotations observed for the condensation of glucose with glycerol are plotted against time. An unexpected feature, which comes to light, is that the minimum rotation does not appear

FIG. 2.

Solutions contain 80 *c.c. of glycerol and* 1·5 *grams of hydrogen chloride.*



to depend on the amount of hydrogen chloride present. The reaction product in each case was the glycerol glucoside described above, as shown by the identical behaviour on methylation and subsequent hydrolysis. It was also found that on long standing the optical activity of an acid solution of glucose in glycerol reverts approximately to its original value, apparently owing to the condensation being reversed as a result of secondary reactions between the solvent and the acid. The slow speed of the condensation led to the investigation being extended to cases where glucose and fructose were dissolved in acid glycerol with the view of ascertaining if, under these conditions, the two sugars combined in whole or in

part. In this connexion it was necessary to perform a series of control experiments with solutions in glycerol of fructose alone. In A (Fig. 2) the specific rotation of fructose dissolved in glycerol containing 1·5% of anhydrous hydrogen chloride is plotted against time; the behaviour of glucose under the same conditions is shown in B (Fig. 1), while in C the ordinates are the algebraic mean of the corresponding ordinates in A and B. The latter curve predicts the behaviour of solutions containing both glucose and fructose, assuming that the sugars do not react with each other, and the actual experimental observations are summarised in D. The values obtained tend to be more lævorotatory than the calculated values, and this was general for all concentrations of the acid reagent employed. Eventually it was found that this discrepancy was due to the varying quantities of water formed by the condensation of the sugars with the solvent and to the effect this produced in the optical activity of fructose solutions. E records the observations made on a solution of fructose in glycerol which had not been rendered anhydrous, whilst in the experiment represented by F the amount of water has been reduced by restricting the total concentration of sugars present in the solution to 3%. The close agreement of F with C indicates that, under the experimental conditions outlined, the behaviour of glucose is not affected by the presence of fructose. This conclusion was supported by the results obtained from an estimation of the reducing power of the above systems. For concentrations of the sugars up to 3% by weight, the percentage loss in reducing power was found to be independent of the concentration. It therefore follows that, in a solution containing both sugars, condensation of one sugar with the other will cause the total reducing power of the mixture to be less than the sum of the reducing powers of the individual sugars. No such diminution was recorded, although the degree of accuracy was such that condensation even to the extent of 5% would have been readily detected. Taking the combined results into consideration, it is unlikely that glucose or fructose can combine in hydroxylic solvents or that reactions involving the condensation of glucose and glycerol play a part in natural processes.

As already indicated, it has proved necessary for the purposes of the research to ascertain which isomeric form of dimethyl glycerol is produced when hexamethyl glycerol glucoside is hydrolysed, and it became evident that the complete series of methylated glycerols should be standardised in view of future work in natural glycerides. The processes developed in this laboratory for determining the constitution of carbohydrates are equally applicable to the structural problems of the natural fats, including the mixed glycerides

Methylation of partly hydrolysed fats followed by hydrolysis should give partly methylated glycerols the constitution of which would lead directly to that of the parent compound. As α-methyl glycerol has already been fully described (J., 1915, **107**, 337), this compound has not been re-examined, but we have prepared αβ-dimethyl glycerol by the action of sodium methoxide on allyl alcohol dibromide and determined the constants of the pure liquid. In order further to characterise the compound, it has been used as a solvent in which the specific rotation of active solutes was determined. As an additional method of identifying the ether it was converted into γ-benzoyl-αβ-dimethyl glycerol and αβ-dimethyl glycerol malate, of which the constants were determined. Attempts to prepare αγ-dimethyl glycerol led to a confusing result. According to Smith (*Z. physikal. Chem.*, 1918, **92**, 717), the product of the action of hydrochloric acid on *epi*chlorohydrin contains nothing but the pure αγ-compound. The αγ-dichlorohydrin prepared by this method gave, however, on treatment with sodium methoxide, a dimethyl glycerol which in all respects was identical with the αβ-dimethyl glycerol described above. The identity was apparent, not only in the ethers, but also in the benzoates and malates prepared from them. Advantage was taken of the fact referred to above that liquid isomerides may frequently be distinguished by the effect they produce on the rotation of active compounds dissolved in them. In this respect also no distinction could be made between the compounds.

Comparison of Dimethyl Glycerols.

	B. p.	n_D.	n_D of benzoate.	$[\alpha]_D^{15°}$ of malate.
αβ-Dimethyl glycerol ...	69·5—70·5°/15 mm.	1·4219	1·5075	−10·48°
Presumed αγ-dimethyl glycerol	70·5—71·5°/18 mm.	1·4219	1·5075	−10·60

Solvent.	Solute.	$[\alpha]_D$.
αβ-Dimethyl glycerol	Ethyl tartrate	+ 11·22°
αγ- ,, ,,	,, ,,	+ 11·19
αβ- ,, ,,	Nicotine	−152·94
αγ- ,, ,,	,,	−153·44

Comparison of the above data leaves no doubt that the compounds are identical and not isomeric. It has not yet been ascertained whether, in this instance, the action of sodium methoxide causes migration of the methyl groups, but the following result suggests that Smith's αγ-dichlorohydrin is interchangeable with the αβ-isomeride. It was expected that β-monomethyl glycerol could be obtained from αγ-dichlorohydrin, which when subjected to methylation by the silver oxide reaction yielded a monomethyl dichlorohydrin. In such a compound, the halogen atoms would

presumably occupy the $\alpha\gamma$-positions, but on heating with an aqueous alcoholic solution of potassium acetate followed by hydrolysis of the acetyl groups the α-monomethyl glycerol described by Irvine and Macdonald (*loc. cit.*) was obtained. The result is comparable with that recorded by Fischer (*Ber.*, 1920, **53**, 1625), who, starting from γ-iodo-$\alpha\beta$-distearyl glycerol, replaced halogen successively by acetyl and hydroxyl and obtained, not $\alpha\beta$-distearyl glycerol, but the $\alpha\gamma$-isomeride.

Trimethyl glycerol was prepared by the continued action of methyl sulphate in alkaline solution on glycerol at 70°. The product formed a constant-boiling mixture with water which distilled at 92°, whilst the distillate formed a homogeneous system with ether. The pure compound was a mobile liquid, b. p. 148°/765·4 mm., $n_D = 1{\cdot}4069$. Ethyl tartrate dissolved in trimethyl glycerol gave $[\alpha]_D = +5{\cdot}99°$.

Experimental.

Preparation of Glycerol Glucoside.—A 5% solution of 20 g. of glucose in anhydrous glycerol containing 0·25% of dry hydrogen chloride was heated in a sealed tube at 100° until it no longer reduced Fehling's solution. The product, isolated on the lines described by Fischer (*loc. cit.*), was a thick syrup containing barium chloride and glycerol. The glucoside was extracted with absolute alcohol and purified by precipitation with ether, but this effected only partial separation of the impurities and the composition was determined through the methylated derivative.

Methylation of Glycerol Glucoside.—Only one typical experiment need be described. The syrup (16 g.) was methylated by the gradual addition of 72 g. of methyl sulphate and 55 g. of sodium hydroxide in 40% solution. The unchanged glycerol was thus converted into trimethyl glycerol, which volatilised during the final heating to 100°. The product (11 g.) was remethylated twice by means of the silver oxide reaction; the refractive index was then constant and on distillation a clear, colourless, mobile liquid was obtained, b. p. 190—192°/12 mm., $n_D = 1{\cdot}4497$ (Found: C, 53·1; H, 8·9. Hexamethyl glycerol glucoside, $C_{15}H_{30}O_8$, requires C, 53·25; H, 8·9%). With this compound, as with many other derivatives of glycerol, analysis by the ordinary combustion process gave variable results. The "wet" process of Simonis and Thies (*Chem. Ztg.*, 1912, **97**, 917) gave, however, satisfactory values for carbon.

Hydrolysis of Hexamethyl Glycerol Glucoside.—A 7% solution of the glucoside in 8% aqueous hydrochloric acid was hydrolysed by heating at 100° for 45 minutes, the course of the reaction being

followed polarimetrically. After neutralisation with barium carbonate, the product was extracted with chloroform and, on distillation of the solvent, crystalline tetramethyl glucose was obtained (yield 65%). After one recrystallisation from light petroleum, the melting point was 88° and a mixed melting point with tetramethyl glucose showed no depression. Evaporation of the light petroleum mother-liquors gave a solid the optical values of which were determined. In one preparation $[\alpha]_D = +75{\cdot}65°$. These results show that the corresponding glycerol γ-glucosides may be present to an extent varying between 0·93 and 1·95%. In order to isolate the methylated glycerol formed during hydrolysis, the aqueous layer was concentrated by distillation through an efficient column. The concentrated solution was extracted with ether and on evaporation of the solvent gave $\alpha\beta$-dimethyl glycerol as a colourless, mobile liquid showing the correct physical constants for this compound.

Polarimetric Examination of the Condensation of Glucose with Glycerol.—The glycerol used was redistilled under diminished pressure, and the finely powdered glucose kept for some days in an evacuated desiccator over sulphuric acid. The sugar (3 g.) was dissolved in glycerol by heating at 90° for 2 hours, the solution when cold showing a specific rotation of 52·3° and a reducing power equivalent to the glucose it contained. Dry hydrogen chloride was drawn into the solution until the necessary increase of weight was obtained (8—10 minutes), and a further 15—20 minutes elapsed before the turbidity of the liquid had decreased sufficiently to make possible even a rough determination of its optical rotation. The following typical results are recorded, the complete figures being embodied in the curves shown in the introduction.

Observed rotations: $l = 1$, $t = 15°$. Conc. of glucose, 3%.

HCl 1%.		HCl 1·5%.		HCl 1·63%.		HCl 2%.		HCl 2·53%.		HCl 3%.	
Hrs.	α.	Hrs.	α.	Hrs.	α.	Hrs.	α.	Hrs.	α.	Hrs.	α.
0	1·95°	0	1·95°	0	1·95°	0	1·95°	0	1·95°	0	1·95°
1	1·7	1·5	1·7	2·25	1·35	2·5	1·2	2	1·15	1	1·1—1·4
2	1·6	2·5	1·3	3	1·3	3·75	0·95	2·5	1	1·75	0·8
10	1·3	4	1·2	4	1·15	5	0·8	4	0·8	3	0·6
26·5	1·0	5·5	1·0	9	0·9	6	0·8	5·5	0·7	4	0·7
48	0·75	7·5	0·8	20	0·55	7·5	0·7	20	0·6	7·5	0·7
		10	0·7			9·5	0·7	29	0·7	9	0·7
		23	0·6			33·5	0·5	44	1·0	23	0·65
						73·5	0·8	53	1·1		
						144	1·1	260	1·8		
						400	1·8				

The reversion of the rotation to practically the initial value is clearly evident in the experiments with 2% and 2·53% HCl, while the minimum specific rotation in all cases is about 15°.

Condensation of Glucose with Glycerol in presence of Fructose.—The optical behaviour of solutions containing glucose and fructose in acid glycerol was studied by methods similar to those described in detail in the case of glucose alone. Solutions containing equal weights of both sugars dissolved in anhydrous glycerol possessed initially a specific rotation of − 21° to − 22°, the corresponding value for the ketose alone being from − 96° to − 97°. Dry hydrogen chloride was then introduced as already described until the acid concentration was 1·5%.

	C.c. of Fehling's solution.	
	Initially.	After 23 hours.
10·3 G. of 3% glucose solution reduced	60	21·5
10·3 G. „ fructose solution reduced	60	1·5
Sum of final reducing powers		23
10·6 G. of 3% glucose–3% fructose solution reduced	120	22·6
10·15 G. of 1·5% glucose solution reduced	30	10·2
10·15 G. „ fructose solution reduced	30	0·5
Sum of final reducing powers		10·7
10·3 G. of 1·5% glucose–1·5% fructose solution reduced	60	10·3

Observed Rotations : $l = 1, t = 15°$.

In each case the sugars were dissolved in 100 g. or 80 c.c. of glycerol.

No. 1. Fructose 3%, HCl 1·5%.

Hours	0	1·25	2	3·25	5·5	8·5	19	23
α	− 3·6°	− 1·25°	− 1·2°	− 1·3°	− 1·5°	− 1·7°	− 2·2°	− 2·4°
$[\alpha]_D$	−96°	−33·3°	−32°	−34·7°	−40°	−45·3°	−58·7°	−64°

No. 2. Fructose 1·5%, HCl 1·59%.

Hours	0	2·5	3·25	4	5·5	10	21
α	− 1·8°	− 0·7° ?	− 0·65°	− 0·65°	− 0·7°	− 0·85°	− 1·1°
$[\alpha]_D$	−96°	−37·3° ?	−34·7°	−34·7°	−37·3°	−45·3°	−58·7°

No. 3. Glucose 3%, fructose 3%, HCl 1·5%.

Hours	0	1	2	3	4	6	8	22·5
α	− 1·6°	+ve.	− 0·2°	− 0·4°	− 0·5°	− 1·4°	− 1·5°	− 2·4°
$[\alpha]_D$	−21·3°	+ve.	− 2·7°	− 5·3°	− 6·7°	−18·7°	−20°	−32°

No. 4. Glucose 1·5%, fructose 1·5%, HCl 1·5%.

Hours	0	2	2·75	3·5	4·3	6	10	21·5
α	− 0·8°	+ 0·2°	+ 0·1°	+ 0·05°	0·0°	− 0·25°	−0·45°	−0·85°
$[\alpha]_D$	−21·3°	+ 5·3°	+ 2·6°	+ 1·3°	0·0°	− 6·5°	−12°	−22·7°

No. 5. Fructose 3%, HCl 1·5%, moisture.

Hours	0	0·5	0·75	1·0	1·5	2	3	5
α	− 3·6°	− 1·0°	− 1·0°	− 1·0°	− 0·8°	− 1·1°	− 1·4°	− 1·6°
$[\alpha]_D$	−96°	−26·7°	−26·7°	−26·7°	−21·3°	−29·3°	−37·3°	−42·7

Hours	9	23
α	− 2·2°	− 3·0°
$[\alpha]_D$	−58·7°	−80·0°
	Blackening.	

αβ-Dimethyl Glycerol.—αβ-Dibromohydrin was prepared by Michael and Norton's method (*Amer. Chem. J.*, 1880, **2**, 18), 20 g. of allyl alcohol giving 51·4 g. of product, b. p. 110—112°/15 mm. To this were added 11 g. of sodium dissolved in methyl alcohol. Sodium bromide was immediately deposited. The reaction proceeded slowly initially, but afterwards suddenly became very rapid, the methyl alcohol boiling vigorously. (It is possible to control the reaction if the solutions are dilute and the mixture is kept initially in ice-cold water for several hours. Completion of the reaction is ensured by heating for a considerable time, as otherwise it is extremely difficult to remove the last traces of bromine.) After neutralisation with carbon dioxide, the *dimethyl glycerol* was extracted with ether and distilled as a clear, colourless liquid, b. p. 69·5—70·5°/15 mm., n_D 1·4219, $d_4^{15°} = 1·016$ $[R_L]_D$ 30·02. Dimethyl glycerol, $C_5H_{12}O_3$, requires $[R_L]_D$ 30·10 (Found : C, 49·4; H, 9·8. $C_5H_{12}O_3$ requires C, 50·0; H, 10·0%). $[\alpha]_D^{15°}$ of ethyl tartrate and nicotine in αβ-dimethyl glycerol as solvent = + 11·22° ($c = 13·37$) and − 152·94° ($c = 13·46$), respectively.

γ-Benzoyl αβ-Dimethyl Glycerol.—The benzoate was prepared by the standard method. Dimethyl glycerol (3·6 g.; 1 mol.) was acted on by 7·5 g. of benzoyl chloride (1·67 mols.) and 2·9 g. of sodium hydroxide (2·5 mols.) in 10% solution at + 5° to − 5°. The product, isolated by extraction with ether, was a fairly mobile oil, b. p. 162°/12 mm., n_D 1·5075 (Found : benzoic acid, 50·0. Benzoyl dimethyl glycerol, $C_{12}H_{16}O_4$, requires benzoic acid, 54·5%).

αβ-Dimethyl Glycerol Malate.—Malic acid (4 g.; 0·6 g. in excess of 1 mol.) was esterified with 6 g. of dimethyl glycerol in presence of gaseous hydrogen chloride at room temperature. The product was poured into a large quantity of water, neutralised with barium carbonate, filtered, and the filtrate extracted with ether for several hours. The ethereal solution was dried, the solvent evaporated, and the residue distilled (yield 5·6 g.). The ester, b. p. 200°/0·5 mm., is a viscous oil, insoluble in water or alcohol but readily dissolved by chloroform. $[\alpha]_D^{15°}$ in chloroform = − 10·60° ($c = 9·05$).

Attempted Preparation of αγ-Dimethyl Glycerol.—αγ-Dichlorohydrin was obtained in the manner described by Smith (*loc. cit.*), b. p. 175·5—176°/733 mm., $n_D = 1·4827$, whilst the treatment with sodium methoxide was carried out as in the case of the αβ-isomeride. The identity of the product with αβ-dimethyl glycerol is referred to in the introduction.

β-Monomethyl αγ-Dichlorohydrin.—αγ-Dichlorohydrin (11·3 g.; 1 mol.) was dissolved in 56·8 g. of methyl iodide (4 mols.) and methylated in the usual manner by the addition of 46·4 g. of silver oxide (2 mols.). The reaction, which was spontaneous, was

continued by warming on a water-bath under a reflux condenser for 8 hours, an additional 10 c.c. of methyl iodide being added when the mixture became pasty. Ether was used as the extracting agent. The product was a clear, colourless liquid (11 g.), b. p. 58°/14 mm., n_D 1·4560 (Found: Cl, 49·7. Monomethyl dichlorohydrin, $C_4H_8OCl_2$, requires Cl, 49·65%).

Attempted Preparation of β-Monomethyl Glycerol.—β-Monomethyl αγ-dichlorohydrin (18·3 g.; 1 mol.) was heated in 36 c.c. of an aqueous alcoholic solution of 29 g. of potassium acetate (2 mols. and 15% excess) in a sealed tube at 120—140° for 12 hours. The potassium chloride that separated was removed, the filtrate evaporated to dryness, and the residue extracted with ether. On distillation of the ether, monomethyl glycerol diacetate remained. This was hydrolysed by boiling with barium hydroxide solution for an hour, neutralising with carbon dioxide, and taking to dryness. The monomethyl glycerol was extracted with chloroform and distilled. The product undissolved by ether was also extracted with chloroform and yielded a further quantity of monomethyl glycerol which had been produced by hydrolysis during the heating process. The monomethyl glycerol obtained was the α-, and not the β-, form; b. p. 110—112°/11 mm., n_D 1·4462 (Found: C, 45·2; H, 9·4. $C_4H_{10}O_3$ requires C, 45·3; H, 9·4%).

Trimethyl Glycerol.—The methyl sulphate reaction was the most satisfactory in the case of glycerol and one typical preparation is described. To 20 g. of glycerol (1 mol.) were added, drop by drop, 186 c.c. of methyl sulphate (4·5 mols.) and 186·7 g. of sodium hydroxide in 40% solution. At first the usual method of procedure was adopted, the methylating reagents being allowed to react with the glycerol at 60—70°, the excess of methyl sulphate being destroyed by heating to 100°. Under these conditions, however, the yield of methylated glycerol was very small. Afterwards the reaction was carried out in a flask provided with a mercury seal and attached to a condenser; trimethyl glycerol and water then formed a volatile mixture which boiled vigorously during the final heating at 100°. The following process was therefore adopted: After destruction of the excess of methyl sulphate the mixture was heated in a brine bath; a mixture of water and trimethyl glycerol distilled steadily at 92°. This was saturated with sodium chloride and extracted with ether. On drying the ethereal solution with calcium chloride a large aqueous layer separated, showing that ether, water, and trimethyl glycerol form a homogeneous system. The ethereal layer was separated from the calcium chloride solution, dried over solid caustic soda, and finally over sodium wire. This treatment has the added advantage of eliminating traces of partly substituted

glycerols. Pure *trimethyl glycerol* was thus obtained as a mobile, refractive liquid, b. p. 148°/765·4 mm., $n_D^{15^\circ}$ 1·4069, $d_4^{15^\circ}$ 0·9401, $[R_L]_D$ 35·06. Trimethyl glycerol, $C_6H_{14}O_3$, requires $[R_L]_D$ 34·84 (Found: C, 53·3; H, 10·2. $C_6H_{14}O_3$ requires C, 53·7; H, 10·45%).

Great difficulty was experienced in the analysis of the methylated glycerols and, although many variations of the usual combustion process have been employed, the results obtained are not yet entirely satisfactory. The figures are, however, sufficiently close to the calculated values to show that each of the compounds possesses the composition ascribed to it. Determination of the methoxyl content by Zeisel's method leads, as has already been pointed out in the case of the α-monomethyl ether (Irvine and Macdonald, *loc. cit.*), to the formation of *iso*propyl iodide in varying amount and therefore cannot be regarded as an accurate analytical factor. For purposes of comparison, the rotatory power of ethyl tartrate in trimethyl glycerol was ascertained. $[\alpha]_D^{15} = 5{\cdot}99$ ($c = 13{\cdot}36$).

The authors desire to acknowledge their indebtedness to the Food Investigation Board and to the Carnegie Trust for the facilities provided during the foregoing research. They also take this opportunity of expressing their gratitude to Principal Sir James C. Irvine, C.B.E., F.R.S., for the invaluable help which he has given.

The University, St. Andrews. [*Received, October 8th*, 1925.]

NOTES.

Sulphonation of 4-Chlorophenol. By John Mildred Gauntlett and Samuel Smiles.

The structure of the acid obtained by sulphonating 4-chlorophenol was determined in the following manner. 4-Aminoanisole-2-sulphonic acid (Bauer, *Ber.*, 1909, **42**, 2110) was converted into 4-chloroanisole-2-sulphonic acid. The chloride of this acid was identical with that obtained by treating 4-chloroanisole with cold chlorosulphonic acid. The same sulphonic acid was obtained by methylating the product from the interaction of 4-chlorophenol with warm fuming sulphuric acid (20% SO_3).

Sodium 4-chloroanisole-2-sulphonate, $MeO{\cdot}C_6H_3Cl{\cdot}SO_3Na$, separates from hot water in prisms containing $2H_2O$, which are lost at 120° (Found: Cl, 14·7; S, 13·2; Na, 9·4. $C_7H_6O_4ClSNa$ requires Cl, 14·5; S, 13·1; Na, 9·4%). *4-Chloroanisole-2-sulphonyl chloride*, $MeO{\cdot}C_6H_3Cl{\cdot}SO_2Cl$, melts at 104° (Found: Cl, 29·3; S, 13·8.

$C_7H_5O_3Cl_2S$ requires Cl, 29·4; S, 13·3%), and the corresponding *amide* at 154°. 4-*Chloroanisole-2-sulphinic acid*, $MeO{\cdot}C_6H_3Cl{\cdot}SO_2H$, prepared from the chloride and aqueous sodium sulphite, has m. p. 116° (Found: C, 40·8; H, 3·5. $C_7H_7O_3ClS$ requires C, 40·7; H, 3·4%). 4-*Chloroanisole-2-methylsulphone*, $MeO{\cdot}C_6H_3Cl{\cdot}SO_2Me$, prepared from the sodium sulphinate and methyl sulphate, separates from hot water in plates, m. p. 94° (Found: C, 43·5; H, 4·1. $C_8H_9O_3ClS$ requires C, 43·5; H, 4·1%). 4-*Chloroanisole-2-disulphoxide*, $(MeO{\cdot}C_6H_3Cl)_2S_2O_2$, was obtained from the sulphinic acid and dilute hydriodic acid, m. p. 124—125° (Found: C, 44·0; H, 3·3. $C_{14}H_{12}O_4Cl_2S_2$ requires C, 44·3; H, 3·2%). 4-*Chloroanisole-2-mercaptan*, $MeO{\cdot}C_6H_3Cl{\cdot}SH$, obtained from the sulphonic chloride by reduction with tin and hydrochloric acid, formed small plates from alcohol, m. p. 42°, which are volatile with steam (Found: C, 48·4; H, 4·0. C_7H_7OClS requires C, 48·1; H, 4·0%). 4-*Chloroanisole 2-disulphide*, $(MeO{\cdot}C_6H_3Cl)_2S_2$, formed colourless needles from alcohol, m. p. 105° (Found: C, 48·3; H, 3·4. $C_{14}H_{12}O_2Cl_2S_2$ requires C, 48·4; H, 3·4%).—King's College, London. [*Received, October 3rd*, 1925.]

2-m-*Xylidino-5-ethoxy*-4 : 5-*dihydrothiazole*. By Vishvanath Krishna Nimkar and Frank Lee Pyman.

Marckwald (*Ber.*, 1892, **25**, 2355) states that acetalyl-*m*-xylylthiocarbamide yields on treatment with strong sulphuric acid a base, $C_{13}H_{20}O_2N_2S$, m. p. 94—95°, giving a picrate,

$$C_{13}H_{18}ON_2S,C_6H_3O_7N_3,$$

m. p. 143—144°. Burtles, Pyman, and Roylance (this vol., p. 581) confirmed the composition of the picrate, for which they found the m. p. 142—143° (corr.), but did not obtain the base in a crystalline state. They expressed the opinion that if Marckwald's analyses were correct the base contained a molecule of water of crystallisation. After several months, the base regenerated from the picrate isolated by Burtles, Pyman, and Roylance became crystalline and separated from alcohol in large prisms, m. p. 102—103° (corr.), which were anhydrous (Found: C, 62·6, 62·4; H, 7·0, 7·3; N, 11·3. $C_{13}H_{18}ON_2S$ requires C, 62·4; H, 7·2; N, 11·2%). The base has, therefore, the expected composition, $C_{13}H_{18}ON_2S$, and is doubtless 2-*m*-xylidino-5-ethoxy-4 : 5-dihydrothiazole. The picrate prepared from the pure base had m. p. 152—154° (corr.) (Found: C, 47·5; H, 4·4. Calc., C, 47·6; H, 4·4%), and it thus appears that neither base nor picrate had been obtained previously in a pure state.—Municipal College of Technology, University of Manchester. [*Received, September 30th*, 1925.]

CCCLXXVI.—*The Heat of Combustion of Salicylic Acid.*

By Endre Berner.

Benzoic acid, naphthalene, and sucrose are the substances generally used for the determination of the heat capacity of a bomb calorimeter. A number of recent excellent investigations have shown, however, that only benzoic acid fulfils the requirements of a calorimetric standard. This acid, therefore, has been accepted as the sole standard substance for calorimetric work; its heat of combustion has been fixed at 6324 calories (15°) per gram weighed in air or 6319 calories (15°) per gram (vac.) ("Comptes Rendus de la Troisième Conférence Internationale de la Chimie," Lyon, 1922, p. 54).

International acceptance of one or more other substances as secondary standards is highly desirable, because the use of a single substance involves a certain risk of introducing an error in the value of the heat capacity of a calorimeter.

Verkade and Coops (*Rec. trav. chim.*, 1924, **43**, 561) recently proposed salicylic acid as a secondary standard substance. They determined its heat of combustion and tested its applicability as a thermochemical standard, but, unfortunately, they failed to take the precautions necessary to secure the utmost purity of their samples.

The author has now determined the heat of combustion of the pure acid. Three different preparations of salicylic acid (Merck, Kahlbaum, and von Heyden) were separately purified, partly by crystallisation from different solvents and partly by sublimation in a vacuum, until the heats of combustion of the products were constant; the values obtained, 5233·8, 5233·8, and 5233·9 cal. (15°) per gram (vac.), were identical within the limits of experimental error.

From the results of twenty experiments made with these samples, the mean value 5233·8 cal. (15)° per gram (vac.) was found for the heat of combustion of salicylic acid at constant volume. To this corresponds the value 5237·4 cal. (15°) per gram weighed in air against brass weights. The ratio of the heats of combustion of benzoic acid and salicylic acid is 6319/5233·8 = 1·2073 (vac.).

Verkade and Coops (*loc. cit.*, p. 571) found a slightly higher value for the heat of combustion of salicylic acid, *viz.*, 5238 cal. (15°) per gram (vac.), and consequently the ratio 1·2066. The discrepancy may be due to an error in the heat capacities of the calorimeters or to a difference in purity of the acids. The first explanation is highly improbable, because both Verkade and Coops and the author used

benzoic acid from the Bureau of Standards, Washington, for the calibration of their calorimeters and obtained almost the same value [V. and C., 5238·1; B., 5237·1 cal. (15°) per gram (vac.)] for the heat of combustion of Merck's salicylic acid (" Präparate von bestimmter Verbrennungswärme "). Verkade and Coops used salicylic acid from four different sources. Because the heats of combustion of those preparations all agreed and one of them—Merck's—gave the same value after a single recrystallisation from ether, the authors contend that their preparations were " absolutely pure." These facts, however, are of no practical value as proofs of the purity of their preparations.

The combustion of salicylic acid (about 0·80 g.) in oxygen at a pressure of 35, 30, or 25 atmospheres is complete; neither carbon monoxide nor the slightest trace of soot nor any smell due to products of incomplete combustion can be detected. Moreover, the acid is neither hygroscopic nor volatile and is easily pressed into pellets which ignite readily. It should therefore be particularly suitable as a standard substance for calorimetric work.

Experimental.

Detailed descriptions of the calorimeter, the method and the experimental results will be published elsewhere.

The calorimeter was of the form recommended by the Bureau of Standards, Washington (*Bull.*, 1915, **11**, 189).

The calorimetric bomb had a thick fixed gold lining and a capacity of about 300 c.c.

Temperature measurements were made with a platinum resistance thermometer. The resistance was measured by Kohlrausch's method (" uebergreifende Nebenschlüsse ") as used by Jaeger and von Steinwehr (*Ann. Physik*, 1906, **21**, 23) and by Fischer and Wrede (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1908, **5**, 129).

The cooling correction, u', was calculated from the formula

$$u' = a\int_{t_1}^{t_2}(u - u_0)dt,$$

in which a is the constant of the calorimeter, u its temperature, u_0 the convergence temperature, and t_1 and t_2, respectively, the time at the beginning and the end of the main period. The numerical value of the integral was in every case determined graphically. In some cases, the cooling correction was also computed by the practical method developed by Dickinson of the Bureau of Standards (*loc. cit.*, p. 229). This method gave practically the same values as those obtained by the complete computation and therefore may be used even in work of high precision.

The total rise of temperature during a combustion was about

1°. The temperature of the jacket was always regulated so that the cooling correction amounted to 2—3 parts in 1000.

The oxygen was prepared from liquid air; it contained very little nitrogen—the correction for nitric acid was 0·5—0·7 cal.—and no combustible impurities. Oxygen from the same source was used for the calibration of the calorimeter and for the combustion of the salicylic acid.

Ignition of the substance was effected electrically by means of a very thin platinum wire; the heat developed by the current was about 0·8 cal. If the wire had been merely pressed into the pellet, ignition sometimes failed to occur. A part of the wire was therefore covered with 0·5—1·5 mg. of benzoic acid by dipping it in the molten acid and placed close against the top of the pellet; under these conditions ignition never failed to take place.

Heat Capacity of the Calorimeter.—This was determined by the combustion of two samples of benzoic acid, (*a*) a standard sample (39b) obtained from the Bureau of Standards, Washington, and (*b*) a sample (517) purified as follows: Benzoic acid (Kahlbaum's "Präparate für kalorimetrische Bestimmungen") was distilled twice at a pressure of 10 mm. of Hg, crystallised twice from benzene and once from carbon disulphide, finely powdered, and dried for 3 days in a vacuum over phosphorus pentoxide.

With 3700 g. of water in the calorimeter vessel, 1 g. of water in the bomb, and an oxygen pressure of 30 atmospheres, the heat capacity was found to be 4066·3 calories (15°) at a mean temperature of 18°. To this value must be added a small correction for the difference in heat capacity of the products of combustion and the oxygen necessary for the combustion. In some recent experiments, the variation of the heat capacity with temperature was determined directly; the heat capacity decreased by about 1 cal. for an increase of 1° at 18°. If the mean temperature during an experiment differed from 18°, a correction for the divergence was applied.

Purification of the Salicylic Acid.—1. Merck's salicylic acid ("Präparate von bestimmter Verbrennungswärme") was finely powdered and dried for 3 days in the way described above (sample 571).

The same preparation was crystallised twice from water and once from chloroform, powdered, and dried for 3 days (sample 571 IIa). It was then dried for 6 days (sample 571 IIb), and sublimed in a vacuum (sample 571 III).

2. Salicylic acid (Kahlbaum D.A.B.5) was crystallised once from water sublimed in a vacuum, crystallised once from chloroform, powdered and dried for 3 days (sample 572 III). This sample was then crystallised once from water, once from benzene, and

once from chloroform, powdered, and dried for 3 days (sample 572 IV).

3. Salicylic acid (von Heyden's "Acidum Salicylicum volum. puriss.") was crystallised twice from water and once from chloroform and dried for 3 days (sample 573 II). This sample was crystallised once from water, once from chloroform, and dried for 3 days (sample 573 III).

TABLE I.

Benzoic Acid.

p = pressure of oxygen in atms.; h = heat capacity, in cal. (15°), of the calorimeter at 18° and 30 atms. of oxygen; d = deviation from the mean heat capacity in parts per 10,000.

Sample.	p.	h.	d.	Sample.	p.	h.	d.
39*b*	30	4066·7	+1·0	517	40	4066·6	+0·7
,,	,,	4065·6	−1·7	,,	30	4065·8	−1·2
,,	,,	4066·7	+1·0	,,	,,	4066·6	+0·7
,,	35	4065·2	−2·7	,,	,,	4066·2	−0·2
517	30	4066·9	+1·5	,,	,,	4066·9	+1·5
					Mean	4066·3	

TABLE II.

Salicylic Acid.

p = Pressure of oxygen = 35 atms.; t = mean temperature; Q = heat of combustion per gram (vac.) in cal (15°); D = deviation from mean heat of combustion in parts per 10,000.

Salicylic acid (*Merck*).

Sample.	t.	Q.	D.
571	18·0°	5237·3	+0·4
,,	18·3	5237·3	+0·4
,,	18·0	5236·4	−1·3
,,	18·1	5237·0	−0·2
,,	18·1	5237·3	+0·4
	Mean	5237·1	

Salicylic acid (*von Heyden*), *purified.*

Sample.	t.	Q.	D.
573 II	18·8°	5234·3	+0·8
,,	17·9	5233·1	−1·5
573 III	18·0	5234·4	+1·0
,,	17·9	5234·7	+1·5
,,	18·0	5233·2	−1·3
	Mean	5233·9	

Salicylic acid (*Merck*), *purified.*

571 IIa	18·1°	5234·6	+1·5
,,	18·1	5233·3	−1·0
571 IIb	18·2	5233·3	−1·0
,, *	18·1	5233·9	+0·2
,, †	18·0	5232·9	−1·7
571 III	18·1	5234·5	+1·3
,,	18·0	5233·1	−1·3
,,	18·0	5234·4	+1·1
	Mean	5233·8	

Salicylic acid (*Kahlbaum*), *purified.*

572 III	18·2°	5234·1	+0·6
,,	18·2	5233·3	−1·0
,,	18·1	5234·1	+0·6
572 IV	18·5	5233·7	−0·2
,,	18·5	5234·6	+1·5
,,	17·9	5233·0	−1·5
,,	18·0	5233·7	−0·2
	Mean	5233·8	

* p = 30 atms.

† p = 25 atms.

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CCCLXXVII.—*Unstable States of Solutions of Sodium Behenate.*

By Mary Evelyn Laing.

Previous communications from this laboratory were devoted to describing the most stable forms of soap and its solutions. In the case of sodium behenate, it was incidentally noted that the type of solution obtained could be radically affected by suitable treatment. For example, on repeated rapid cooling, the behenate solutions could be obtained at room temperature for a short period as limpid, mobile liquids, whereas slow cooling produced the usual hard, white curd. Reheating the mobile liquid of a $0{\cdot}2N_w$-solution to about 90° produced a clear, stiff, isotropic jelly, which quick cooling once more temporarily rendered fluid. Some of the most interesting solutions could only be kept less than half an hour.

The appearance and behaviour of these solutions and their transitory states have been quantitatively examined.

The task was undertaken by a team of experienced investigators, who worked simultaneously on portions of solutions prepared by Mr. G. M. Langdon. He also made the macroscopic observations. The microscopic study was undertaken by Mr. S. E. Wiltshire, Miss M. E. Kieser carried out the *E.M.F.* experiments, Miss M. E. Laing the freezing-point determinations, Miss K. M. Hay the indicator tests, and Mr. W. C. Quick measured the conductivity.

Sodium behenate solutions were made up in silver tubes by shaking the requisite quantities (Bunbury and Martin, J., 1914, **105**, 417) of standardised alkali with weighed quantities of behenic acid, m. p. 81·0—82·0°, kindly made for us by Messrs. J. C. Crosfield and Sons, Ltd., by the catalytic hydrogenation of Kahlbaum's erucic acid. The homogeneous soaps were transferred to thick-walled glass tubes, which were sealed for optical investigation according to the method previously described (McBain and Langdon, this vol., p. 852). Parallel experiments were carried out with solutions made up in 1913 (McBain and Taylor, *Z. physikal. Chem.*, 1911, **76**, 179). The strengths used were 0·01, 0·05, 0·1, 0·2, $0{\cdot}5N_w$, *i.e.*, mole per 1000 g. of water. The observations here recorded were repeated many times; *e.g.*, a $0{\cdot}1N_w$-solution was alternately heated and cooled twenty times under different conditions and the results were reproducible, the only effect that varied being the number of " flocks " appearing in the mobile liquid.

The stable forms of the behenate solutions at room temperature, with the exception of $0{\cdot}01N_w$, were solid, white, moist curds. Curd formation, however, could be suspended by special heat treatment,

as was well illustrated by the behaviour of a $0{\cdot}05N_w$-solution. On being heated to about 88°, the curded $0{\cdot}05N_w$-solution melted to a fairly mobile, milky liquid containing a few white flakes. If this solution were allowed to cool slowly, more flakes separated and the whole gradually became a network of curd; the transformation from Brownian particles in movement to short and then long fibres could be observed under the ultramicroscope. Photographs of such gradual transitions have been published elsewhere (McBain, Darke, and Salmon, *Proc. Roy. Soc.*, 1921, *A*, **98**, 395; Bogue, "Colloidal Behaviour," Vol. I, pp. 410—429; *Nature*, 1921, **107**, 45; Alexander, "Colloid Chemistry, Theoretical and Applied," Vol. I, 1925).

On cooling rapidly, the white flakes, which formed at about 75°, rose to the surface, leaving a clear lower layer. On heating to 90°, these flakes melted and the system consisted of two clear layers. As the tube cooled again, curding took place in two stages, the upper layer solidifying at 75° and the clear lower layer after some hours at room temperature.

The quantitative investigation had to be carried out as quickly as possible, before the homogeneous, mobile liquid produced by rapid cooling set to a mass of curd fibres.

The hydroxyl-ion concentration of the $0{\cdot}05N_w$-solution at 18° was found by *E.M.F.* measurements with the hydrogen electrode to be $0{\cdot}007N_w$ during the first hour, but this value declined to $0{\cdot}0008N_w$ when the clear liquid had solidified to form white curd. The concentration of hydroxyl ions in the mobile liquid was shown by the indicator method, using alizarin yellow G and Sörensen's buffers, to be $0{\cdot}007N_w$ at 90° and slightly higher at room temperature.

The clear $0{\cdot}05N_w$-sodium behenate at 18°, therefore, is hydrolysed to the extent of 14% (= $0{\cdot}007N_w$-OH) and contains $0{\cdot}021N_w$-acid soap expressed in terms of behenate, or $0{\cdot}014N_w$, in terms of sodium; if this is formed, as in the case of the palmitate, according to the equation $3\text{NaBe} + \text{H}_2\text{O} = \text{NaOH} + 2\text{NaBe,HBe}$. Hence 42% of the total behenate radical is in the form of acid soap. This acid soap is colloidal and exerts no osmotic pressure (McBain, Taylor, and Laing, J., 1922, **121**, 621).

The osmotic data were obtained from depressions of the freezing point, determined by the usual Beckmann method, using inoculation; at least four concordant readings were taken before a solution curded. The depression for the $0{\cdot}05N_w$-solution was 0·036°. The hydroxyl ions, present to the extent given above, would correspond to a depression of 0·013° and together with the equivalent sodium ions would account for a depression of 0·026°. The difference, 0·010°, which must be due to that part of the soap in solution as electrolyte, corresponds to 0·0027 g.-mol. of fully dissociated, binary, crystal-

loidal electrolyte. What remains of the total concentration $0{\cdot}05 - 0{\cdot}014 - 0{\cdot}007 - 0{\cdot}0027N_w = 0{\cdot}0263N_w$, must be the concentration of the undissociated neutral colloid. The constituents of this unstable but clear solution, and their concentrations, are very nearly those in Table I.

TABLE I.

Constituents of unstable $0{\cdot}05N_w$-Sodium Behenate at 18°.

1. From *E.M.F.* (OH′)	$0{\cdot}007N_w$		14% hydrolysis alkalinity.
2. Equivalent to Na_2HBe_3	$0{\cdot}0140N_w$	(Na·)	42% acid soap (colloid).
3. From lowering (Na·)=(Be′)+(OH′)	$0{\cdot}0097N_w$		5% dissociated soap.
4. Remainder $(NaBe)_x$	$0{\cdot}0263N_w$	(Na)	53% neutral colloid.

The conductivity data are summarised in Table II. The conductivities of two samples of $0{\cdot}05N_w$-solution were measured at intervals over a period of 20 hours, and that of a $0{\cdot}1N_w$-solution at intervals during 18 hours, after making up. The values recorded for the liquid are the means of those obtained within the first hour, the curd values are those obtained after 18—20 hours.

TABLE II.

Specific Conductivity (κ) of Sodium Behenate Solutions at 18°.

	Unstable liquid.		Final curd.	
Conc. (N_w).	κ.	α%.	κ.	α%.
0·05	$1{\cdot}74 \times 10^{-3}$	15·9	$0{\cdot}311 \times 10^{-3}$	2·8
0·1	$2{\cdot}79 \times 10^{-3}$	12·8	$0{\cdot}42 \times 10^{-3}$	1·9

The degree of dissociation, α, calculated by dividing the actual conductivity found by the molar conductivity of sodium hydroxide at infinite dilution at 18° (*viz.*, 216·5) is 15·9% for the $0{\cdot}05N_w$-solution, a value slightly greater than that (14%) found by *E.M.F.* measurements; the approximate agreement shows that the free hydroxide accounts for most of the conductivity. A more exact comparison may be made by calculating from the data of Table I the specific conductivity of the $0{\cdot}05N_w$-solution at 18°. The products of the concentrations per c.c. of the various ions shown in Table I and their respective mobilities (43·6 for Na·, 172·9 for OH′, and 20·7 for Be′) being added together, the calculated value for the specific conductivity is found to be $1{\cdot}69 \times 10^{-3}$. The agreement with the observed value, $1{\cdot}74 \times 10^{-3}$, is very close, especially in view of the fact that different samples of unstable solutions were taken for these measurements; one sample actually gave the value $1{\cdot}69 \times 10^{-3}$ reciprocal ohm.

Full allowance having been made for the conductivity due to the hydroxyl ions in the final curd, it is evident that the curd fibres, though not in solution (this was shown by analysis of the mother-

liquor squeezed out from such curds), contribute to the residual conductivity. This is apparently due to the free ions of the electrical double layer of the very extensive surface of the fine fibres (compare Laing, *J. Physical Chem.*, 1924, **28**, 673; Laing and McBain, J., 1920, **117**, 1507). The data show that these supercooled solutions are highly unstable, the extent of hydrolysis being many times greater even than that for the solutions at 90°. At the lower temperature, after a short time, the hydrolysis diminishes to a tenth of its value and the equilibrium shifts in favour of the formation of insoluble sodium behenate, which separates in curd form from the solution. It seems possible that in the initial clear liquid the acid soap may peptise the neutral soap. Solutions of acid soap froth freely (McBain, Taylor, and Laing, *loc. cit.*).

The $0{\cdot}1N_w$-behenate solution in the unstable condition was similar to the $0{\cdot}05N_w$-solution, but was less hydrolysed. The concentration of hydroxyl ions due to hydrolysis was shown by the hydrogen electrode to be $0{\cdot}0098N_w$ or 9·8% (afterwards falling to $0{\cdot}0012N_w$ when the clear liquid had set to a white curd). The depression of the freezing point was 0·035°. This would be fully accounted for by the free sodium hydroxide, but, as is seen from Table II, there is still a small amount of conductivity to be accounted for as in the case of the $0{\cdot}05N_w$-solution.

The macroscopic and the microscopic behaviour of the $0{\cdot}1N_w$-solution are just like those of the $0{\cdot}05N_w$-solution described above, except that the instability increases with concentration.

The $0{\cdot}2N_w$-solution was too unstable to permit of freezing-point determinations. This solution is very viscous and difficult to prepare. It exhibited, however, a remarkable change in viscosity. The melted curd was a clear, isotropic jelly at 90°, but, on cooling, the gel "melted" to a mobile, cloudy liquid. We have observed this curious phenomenon of gelation at a relatively high temperature and fluidity at a low temperature in only one other instance, namely, in a solution of nitro-cotton in alcohol; this is a clear, elastic jelly at room temperature and a mobile fluid at the temperature of liquid air (observation by Mr. L. E. Smith in this laboratory).* This observation can be readily explained on the basis of the theory of neutral colloids put forward by McBain (*Trans. Faraday Soc.*, 1924, **20**, 22).

The hydroxyl-ion concentration of the $0{\cdot}2N_w$-solution is $0{\cdot}005N_w$, indicating a hydrolysis alkalinity of only 2%. This value corresponds exactly with that found by the indicator method. Most of the soap of the $0{\cdot}2N_w$-solution must be present as insoluble, undissociated, neutral colloid.

* Compare Szegvari (*Kolloid-Ztg.*, 1924, **34**, 34), who, however, used a more complicated mixture of solvent and non-solvent.

Whether cooled rapidly or slowly, the $0{\cdot}5N_w$-solution of sodium behenate forms curd at room temperature. It is a highly viscous gel at 90°.

It appears that ease of curding increases with rise of viscosity, which takes place whenever separated matter (shown by streakiness) is present, or upon lowering of temperature. Curd also forms more rapidly after the solution has been heated in glass.

A sodium behenate solution separates into two layers on addition of $0{\cdot}4N_w$-sodium chloride; whereas in the case of sodium palmitate of the same concentration, twice this quantity of salt is required to produce the same change. The salted-out system, $0{\cdot}05\ N_w$-NaBe + $0{\cdot}42N_w$-NaCl, and also $0{\cdot}05N_w$-NaBe + $0{\cdot}59N_w$-NaCl, becomes homogeneous at 100°. This temperature is above that, 72—75°, at which the corresponding palmitate–sodium chloride system becomes homogeneous. Both facts are in accordance with the insolubility of sodium behenate at low temperatures.

Neutral behenate solutions, in the absence of sodium chloride, were never observed to separate spontaneously into two layers on standing at high temperatures, as is the case with acid sodium palmitate ($0{\cdot}4N_w$-NaP, $0{\cdot}1N_w$-HP). In appearance, the acid salts of behenic and palmitic acids are very similar.

On reviewing the behaviour of these colloidal behenate systems, one is struck by their analogy with certain crystalloidal systems. When, for example, barium sulphate is produced rapidly from a mixture of barium chloride and a sulphate, a highly supersaturated solution may be obtained which deposits matter in the colloidal state. On sudden cooling of the behenate solutions, supersaturation with respect to neutral colloid sets in and similar amorphous, flocculent material is formed. Thus on cooling of either system, colloid or crystalloidal, one gets separation of (crystalline) curd fibres on the one hand and of true crystals on the other. On standing in contact with their respective mother-liquors, colloidal barium sulphate crystallises and colloidal sodium behenate curds.

Summary.

(1) Although the stable form of $0{\cdot}05$—$0{\cdot}5N_w$-sodium behenate at room temperature is a hard, white curd, these solutions can be obtained temporarily as clear, very mobile liquids, which are hydrolysed to an abnormally large extent.

(2) The largest constituent of the unstable mobile solutions is neutral undissociated colloid, the next largest being colloidal acid sodium soap with the equivalent quantity of free sodium hydroxide. There is only a very small proportion of dissociated soap.

UNIVERSITY OF BRISTOL. [*Received, July 24th*, 1925.]

CCCLXXVIII.—*Sulphur Compounds Removed from a Persian Petroleum by Means of Sulphuric Acid. Part I.*

By Edward Henry Thierry.

Mabery and Smith (*Amer. Chem. J.*, 1891, **13**, 232) isolated several organic sulphur compounds from a crude Ohio oil and established the presence of a series of dialkyl sulphides. Mabery and Quayle (*ibid.*, 1906, **35**, 404) obtained very different results during an investigation of a Canadian petroleum, a series of saturated cyclic compounds, named thiophanes, of the empirical composition $C_nH_{2n}S$ being isolated; the actual compounds ranged from $C_7H_{14}S$ to $C_{18}H_{36}S$ and a derivative of the substance $C_6H_{12}S$ also was prepared (see also von Braun and Trümpler, *Ber.*, 1910, **43**, 543; Trochimovski, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 880). More recently, other workers have described the isolation and identification of thiophen and its homologues in shale oil.

The product now investigated was a sulphuric acid sludge from the refining of Persian petroleum kindly supplied by Mr. Kewley of the Asiatic Petroleum Co. The oil that separated on dilution was carefully fractionated and of the twenty-nine fractions boiling below 120°/125 mm., four have been investigated. Three of these consisted essentially of methyl ethyl sulphide, tetra- and penta-methylene sulphides. The fourth fraction was a mixture. It contained a compound $C_4H_{10}S$; this was not diethyl sulphide, but sufficient material was not available to determine whether it was methyl propyl sulphide or methyl *iso*propyl sulphide. All the fractions had an intense odour, but the purest samples of the cyclic sulphides were in no sense objectionable. The various compounds have been characterised by the preparation of a number of derivatives such as sulphonium iodides and double salts with mercuric salts.

Experimental.

The dark supernatant oil obtained by greatly diluting the sulphuric acid sludge (12 litres) with water was shaken with sodium hydroxide and dried over sodium sulphate; a further quantity was extracted from the diluted liquid with chloroform, the total yield being 1800 c.c. The oil was distilled and the more volatile portions were fractionated five times at a pressure of 760 mm.; the fractions obtained were: (1) below 50°, 0·5 c.c.; (2) 59—64°, 90 c.c.; (3) 64—68°, 11 c.c.; (4) 68—70°, 23 c.c.; (5) 70—80°, 10 c.c.; (6) 80—89°, 8 c.c.; (7) 89—92°, 11 c.c.; (8) above 92°, 7 c.c.

The oils boiling above 100°/760 mm. were fractionated eleven times at 125 mm. Table I shows the degree of separation achieved.

TABLE I.

Fraction.	B.p./125 mm.	C.c.	Fraction.	B.p./125 mm.	C.c.
9	up to 60°	4	20	90—93°	30
10	60—63	12	21	93—96	12
11	63—66	20	22	96—99	9
12	66—69	3	23	99—102	19
13	69—72	5	24	102—105	28
14	72—75	5	25	105—108	16
15	75—78	10	26	108—111	14
16	78—81	70	27	111—114	35
17	81—84	75	28	114—117	20
18	84—87	10	29	117—120	18
19	87—90	3	Residue (to be examined)		

Fractions 4, 7, 11, and 17 have been carefully examined.

Fraction 4 contained 61% of chloroform. No satisfactory analysis was possible, but the remaining liquid contained about 34·5% S. On shaking with mercuric iodide, decanting, and evaporating in a vacuum, pale yellow crystals were obtained which dissociated very rapidly in the air and softened at 59° (Smiles, J., 1900, **77**, 164, gives m. p. 59° for $CH_3{\cdot}S{\cdot}C_2H_5,HgI_2$). The liquid (2 c.c.) reacted briskly with methyl iodide (1 c.c.) and mercuric iodide (excess). After 3 minutes, the product was washed with ether and crystallised from acetone–ether; it then formed fine yellow needles, m. p. 86° [$(CH_3)_2SI{\cdot}C_2H_5,HgI_2$ has m. p. 86°; Smiles, *loc. cit.*].

White crystals of *methyl ethyl sulphide mercurichloride* were immediately precipitated on addition of alcoholic mercuric chloride to the liquid. Several crystallisations from acetone and water gave rather unstable crystals, m. p. 101—102°.

Most of the mercurihalides here described are unstable and were purified with difficulty, immediately beginning to lose sulphide on exposure to air; the ultimate analyses, therefore, were unsatisfactory. Sintering frequently occurs during melting-point determinations and this, together with the tendency to dissociate, makes trustworthy observations difficult to obtain.

Fraction 7 contained 0·5% of chloroform. The analytical figures found (C, 56·4; H, 11·0) differ from those required for diethyl sulphide (C, 53·3; H, 11·1%), but consideration of the results obtained with fraction 11 makes it very probable that the divergence in both cases is caused by admixture of about 6% of a hydrocarbon, b. p. 100—105°.

The mercuri-iodide, prepared as described under Fraction 4, formed unstable, pale yellow crystals which did not soften below 100°. The methylsulphonium iodide mercuri-iodide formed pale yellow crystals which melted at 54° after repeated crystallisation

from acetone–ether, and the mercurichloride, unstable, white needles, which melted at 68° after repeated crystallisation from acetone by cautious addition of water. Smiles (J., 1900, **77**, 164) gives 52° as the m. p. of $(C_2H_5)_2S,HgI_2$ and 67° as that of $(C_2H_5)_2(CH_3)SI,HgI_2$, whilst for $(C_2H_5)_2S,HgCl_2$ Loir (*Annalen*, 1853, **87**, 369) records m. p. 90° and Abel (*H.*, 1895, **20**, 269) m. p. 119°. These results indicate clearly that the compound is not diethyl sulphide. No addition compounds of the above types of the methyl propyl sulphides have been described.

Fraction 11 was refractionated and the largest fraction, b. p. 64—65°/125 mm., was examined. The liquid boiled at 120—121°/760 mm. (Found: C, 56·6; H, 9·8; S, 34·0%). Di*iso*propyl sulphide (C, 61·0; H, 11·9; S, 27·1%) boils at 120·5°/763 mm. (Beckmann, *J. pr. Chem.*, 1878, **17**, 459), and tetramethylene sulphide (C, 54·5; H, 9·1; S, 36·3%) at 119° (von Braun and Trümpler, *Ber.*, 1910, **43**, 549).

The divergence from the values for tetramethylene sulphide may be ascribed to the presence of a little hydrocarbon, since derivatives were obtained in a pure state with comparative ease.

The *methiodide*, prepared in the usual way, crystallised from alcohol in fine, white needles, decomp. 185—190° (Found: I, 54·6. $C_5H_{11}IS$ requires I, 55·2%). The mercurichloride, crystallised from acetone–water, had m. p. 126° (Trochimovski, *loc. cit.*, gives m. p. 124·5—125·5°). *Tetramethylene sulphide mercuri-iodide*, prepared in the usual way, separated from acetone–water in white crystals, m. p. 58°. *Tetramethylenemethylsulphonium iodide mercuri-iodide*, prepared as previously described, formed yellow crystals, m. p. 111°.

Fraction 17 was refractionated four times; the largest fraction had b. p. 83—84°/125 mm. and 138·5°/742 mm. (Found: C, 58·5; H, 9·8; S, 31·3. Calc. for $C_5H_{10}S$, C, 58·8; H, 9·8; S, 31·4%). Low results for sulphur were obtained unless oxidation was carried out for 15 hours at 180° and then, after the pressure had been released, for 10 hours at 250°. In estimating the carbon and hydrogen, the best results were obtained by weighing the liquid in a small bubbler, which was then fixed to the end of the combustion tube, the passage of the oxygen causing steady evaporation. It seems certain that the compound is pentamethylene sulphide (compare von Braun, *loc. cit.*). The mercurichloride was prepared, and crystallised from benzene.

Pentamethylenemethylsulphonium iodide, prepared in the usual way, was converted into the sulphonium base by means of silver oxide; the solution was exactly neutralised with hydrochloric acid and gently evaporated to small bulk. The crystalline *sulphonium*

chloride obtained on cooling was precipitated from alcoholic solution with ether, washed with acetone, and dried in a vacuum over sulphuric acid. The white crystals thus obtained dissociated without melting on heating and decomposed slightly on long standing (Found: C, 46·7; H, 8·7; Cl, 22·85. $C_6H_{13}ClS$ requires C, 47·2; H, 8·6; Cl, 23·3%).

Pentamethylene sulphone was obtained in very small yield by oxidising the sulphide (2 g.) with excess of permanganate solution; it crystallised from benzene–light petroleum in white plates, m. p. 98°. Trochimovski (*loc. cit.*) gives m. p. 98·5—99°.

Pentamethylene sulphide mercuri-iodide, prepared in the usual way, was washed with ether and crystallised from acetone by cautious addition of water. The white crystals obtained, m. p. 72—74°, dissociated completely within a few hours when exposed to the air. The mercurichloride separated from benzene in white crystals, m. p. 135—136° (Trochimovski gives m. p. 137·5°). The *chloroplatinate* was obtained by adding a few drops of the sulphide to a strong aqueous solution of platinic chloride; the yellow crystals that separated after a few hours were crystallised from acetone–water. [Found: Pt, 35·4. $(C_5H_{10}S)_2PtCl_4$ requires Pt, 36·4%]. *Pentamethylenemethylsulphonium iodide mercuri-iodide*, prepared as previously described, separated from acetone–ether in yellow crystals, m. p. 78°.

The author expresses his thanks to Professor Donnan for suggesting this work and to Professor Collie and Dr. Brady for valuable advice given during its progress.

The Ralph Foster Laboratory of Organic Chemistry,
University College. [*Received, February 26th*, 1925.]

CCCLXXIX.—*Condensations of the Sodium Derivatives of Trimethylene Glycol and Glycerol.*

By Arthur Fairbourne and Graham Edward Foster.

In extension of the work on the condensation of 1-chloro-2 : 4-dinitrobenzene with glycerol (J., 1921, **119**, 1035) and ethylene glycol (*ibid.*, p. 2077), the similar condensation in the case of trimethylene glycol has now been investigated.

A solution of the sodium derivative is readily obtained by dissolving sodium in excess of trimethylene glycol and may be used for effecting the condensation. In spite of the large excess of glycol present, and although monosodium glyceroxide gives rise to only

one product in the corresponding reaction (*loc. cit.*, p. 1037), both mono- and bis-dinitrophenyl ethers of trimethylene glycol are produced, even when the chlorodinitrobenzene is added slowly.

$$\begin{array}{l}CH_2\cdot OH\\ CH_2\\ CH_2\cdot OH\end{array} \longrightarrow \text{(I.)} \begin{array}{l}CH_2\cdot OH\\ CH_2\\ CH_2\cdot O\cdot C_6H_3(NO_2)_2\end{array} + \begin{array}{l}CH_2\cdot O\cdot C_6H_3(NO_2)_2\\ CH_2\\ CH_2\cdot O\cdot C_6H_3(NO_2)_2\end{array} \text{(II.)}$$

The relative yields of these ethers vary with the concentration of the sodium derivative and therefore may be regarded as dependent on the tendency to set up the equilibrium

$$\begin{array}{l}CH_2\cdot O\cdot C_6H_3(NO_2)_2\\ CH_2\\ CH_2\cdot OH\end{array} + \begin{array}{l}CH_2\cdot OH\\ CH_2\\ CH_2\cdot ONa\end{array} \rightleftharpoons \begin{array}{l}CH_2\cdot O\cdot C_6H_3(NO_2)_2\\ CH_2\\ CH_2\cdot ONa\end{array} + \begin{array}{l}CH_2\cdot OH\\ CH_2\\ CH_2\cdot OH\end{array}$$

it being assumed, as in the two previous papers, that the primary condensation involves merely the replacement of the sodium by the substituent group:

$$R\cdot O\cdot Na + Cl\cdot C_6H_3(NO_2)_2 \longrightarrow R\cdot O\cdot C_6H_3(NO_2)_2.$$

On this assumption depend the arguments previously put forward in support of the structure of glycerides (*loc. cit.*, p. 1035). Doubt was cast on its validity, however, by the accidental preparation of the bisdinitrophenyl ether above mentioned and by the further discovery that *tri*-substituted derivatives of glycerol can be obtained by treating monosodium glyceroxide, suspended in an inert solvent, with *one* equivalent of certain acid chlorides, a reaction not contemplated in the previous papers.

$$\begin{array}{l}CH_2\cdot OH\\ 3CH\cdot OH\\ CH_2\cdot ONa\end{array} + 3Ph\cdot SO_2Cl \longrightarrow \begin{array}{l}CH_2\cdot SO_3Ph\\ CH\cdot SO_3Ph\\ CH_2\cdot SO_3Ph\end{array} + \begin{array}{l}CH_2\cdot OH\\ 2CH\cdot OH\\ CH_2\cdot OH\end{array}$$

Moreover, such trisubstituted products were obtained from disodium glyceroxide under identical conditions:

$$3C_3H_6O_3Na_2 + 6Ph\cdot COCl \longrightarrow \begin{array}{l}CH_2\cdot CO_2Ph\\ 2CH\cdot CO_2Ph\\ CH_2\cdot CO_2Ph\end{array} + \begin{array}{l}CH_2\cdot OH\\ CH\cdot OH\\ CH_2\cdot OH\end{array}$$

It was realised that the formation of these substances might be due to direct interaction of labile chlorine atoms and hydroxyl groups,

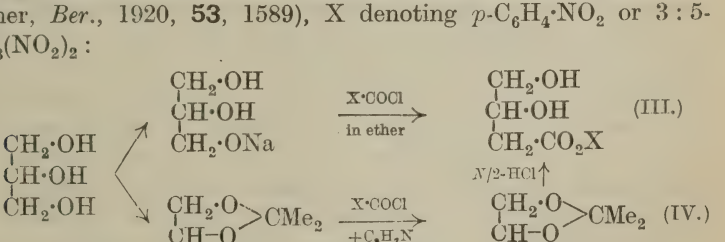
$$\begin{array}{l}CH_2\cdot ONa\\ CH_2\\ CH_2\cdot OH\end{array} + 2Cl\cdot C_6H_3(NO_2)_2 \longrightarrow \begin{array}{l}CH_2\cdot O\cdot C_6H_3(NO_2)_2\\ CH_2\\ CH_2\cdot O\cdot C_6H_3(NO_2)_2\end{array},$$

the excess of the sodium derivative merely serving to destroy the hydrogen chloride thus formed. Glycerol, ethylene glycol, and

trimethylene glycol were therefore heated separately with 1-chloro-2 : 4-dinitrobenzene in presence of calcium carbonate, and trimethylene glycol mono-2 : 4-dinitrophenyl ether was treated similarly in presence of sufficient inert solvent to dissolve all organic matter, but in no case was there a trace of ionisable halogen in the product. It appears clear, therefore, that no condensation between halogen atoms and hydroxyl groups occurs during the reactions with chlorodinitrobenzene, and that the chlorine removes the sodium in the way previously assumed.

The production from sodium glyceroxide of the tri-ester mentioned above might be explicable in the light of Fischer's observation (*Ber.*, 1920, **53**, 1621, 1634) that mono-esters of polyhydric alcohols in ethereal solution in presence of a catalyst such as potassium carbonate or sodium ethoxide are moderately rapidly transformed into di-esters and free alcohols. A similar explanation is untenable, however, in the case of trimethylene glycol bisdinitrophenyl ether, for when the mono-ether was treated with a solution of sodium in trimethylene glycol under the conditions existing during the condensation with chlorodinitrobenzene no bis-ether was found in the product, the very different solubilities of the mono- and bis-ethers in acetic acid rendering the absence of the latter easily provable.

The α-structure of monosodium glyceroxide (*loc. cit.*, p. 1036) has been confirmed by the following series of reactions using *iso*propylidene glycerol (Irvine, Soutar, and Macdonald, J., 1915, **107**, 337; Fischer, *Ber.*, 1920, **53**, 1589), X denoting p-$C_6H_4{\cdot}NO_2$ or 3 : 5-$C_6H_3(NO_2)_2$:



Experimental.

Trimethylene Glycol Mono-2 : 4-dinitrophenyl Ether (I).—Sodium (1·14 g.) was dissolved, in small portions to prevent charring, in 40 c.c. of trimethylene glycol, and the solution was stirred and heated at 100° while a suspension of 10·2 g. of 1-chloro-2 : 4-dinitrobenzene in 30 c.c. of the glycol was gradually added. Heating and stirring were continued until the chlorodinitrobenzene dissolved (½ hour). The product was poured into 1000 c.c. of 20% acetic acid an oil

being precipitated. The whole was boiled for 30 minutes; most of the oil had then redissolved and the remainder had crystallised (A). The solution was filtered, and cooled to 0° after 24 hours. The colourless needles deposited were dried in a vacuum over sulphuric acid and recrystallised from benzene–ligroin (b. p. 40—60°). The *ether* thus obtained (yield 6 g.), m. p. 52°, was soluble in ether, benzene, alcohol, acetone, or acetic acid, and sparingly soluble in water or ligroin (Found: N, 11·5. $C_9H_{10}O_6N_2$ requires N, 11·55%).

The *acetyl* derivative prepared by heating the ether for a few minutes with 2 vols. of acetyl chloride and acetic anhydride (equal parts) and boiling the product with much water, separated from the filtered solution in long, colourless needles, m. p. 85°, the yield being nearly quantitative (Found: C, 46·1; H, 4·45; N, 9·9. $C_{11}H_{12}O_7N_2$ requires C, 46·4; H, 4·25; N, 9·9%).

The *benzoyl* derivative was prepared by shaking a warm mixture of the ether and benzoyl chloride with successive small quantities of 20% sodium hydroxide solution, added in sufficient amount to prevent the orange colour from being discharged; water was then added. The *benzoyl* derivative, obtained as a semi-solid mass on cooling the mixture, separated from alcohol in colourless crystals, m. p. 95°, soluble in most of the common organic solvents (Found: N, 8·2. $C_{16}H_{14}O_7N_2$ requires N, 8·11%).

Trimethylene Glycol Bis-2 : 4-dinitrophenyl Ether (II).—The substance (A) mentioned above was sparingly soluble in alcohol, ether, or acetone, but by recrystallisation from boiling glacial acetic acid the bis-*ether* was obtained in colourless needles (yield 0·5 g.), m. p. 180° (Found: C, 44·0; H, 3·2; N, 13·4. $C_{15}H_{12}O_{10}N_4$ requires C, 44·1; H, 3·0; N, 13·6%).

*Glyceryl Tri-*p*-toluenesulphonate*, $C_3H_5(O{\cdot}SO_2{\cdot}C_7H_7)_3$.—Disodium glyceroxide was prepared by the method of Löbish and Loos (*Monatsh.*, 1881, **2**, 842) (Found: Na, 33·0. Calc., Na, 33·8%).

A mixture of equimolecular proportions of either mono- or di-sodium glyceroxide and *p*-toluenesulphonyl chloride in dry ether or benzene was kept for 24 hours, then boiled under reflux for ¼ hour, and filtered. The *glyceride* obtained on distilling off the solvent slowly solidified, and crystallised from alcohol in colourless needles, m. p. 103° (Found: C, 51·6, 51·8; H, 4·8, 4·8; S, 17·4; *M*, cryoscopic in benzene, 564. $C_{24}H_{26}O_9S_3$ requires C, 52·0; H, 4·7; S, 17·3%; *M*, 554).

Glyceryl tribenzenesulphonate, obtained in a similar way from benzenesulphonyl chloride, crystallised from alcohol in needles, m. p. 80° (Found: C, 49·0; H, 3·9. $C_{21}H_{20}O_9S_3$ requires C, 49·2; H, 3·9%).

Action of Benzoyl Chloride upon Sodium Glyceroxides.—The

products obtained by the action of an ethereal solution of benzoyl chloride on mono- and di-sodium glyceroxides were not identical.

Monosodium glyceroxide yielded α-monobenzoyl glycerol (compare *loc. cit.*, p. 1340).

Disodium glyceroxide yielded tribenzoyl glycerol, which, even after repeated crystallisation from ligroin, melted at 71—72° (Found: C, 71·25; H, 4·95. Calc., C, 71·3; H, 4·95%). The m. p. is given by Skraup (*Monatsh.*, 1889, **10**, 393) as 75—76·5°, by Balbiano (*Ber.*, 1903, **36**, 1574) as 71—72°, and by Krafft (*ibid.*, p. 4341) as 76°. A comparison of these references and others showed that the substance melted at 76° or 72° according as it had been crystallised from alcohol or ligroin. The above product was therefore crystallised from alcohol. It then melted at 76°. Subsequent recrystallisation from ligroin (b. p. 40—60°), or slow solidification of the fused material, reduced it to 72° again.

Action of p-*Nitrobenzoyl Chloride upon Monosodium Glyceroxide.*—Monosodium glyceroxide was treated with an equivalent quantity of *p*-nitrobenzoyl chloride in ethereal solution, and the reaction carried out in the usual manner. The product obtained by filtration and evaporation of the solvent was an oil which solidified on cooling and crystallised from chloroform in needles, m. p. 107°. A mixture of this with a specimen of α-mono-*p*-nitrobenzoyl glycerol (m. p. 107°) prepared by Fischer's method (*Ber.*, 1920, **53**, 1596) also melted at 107°. In the preparation of *iso*propylidene glycerol as an intermediate product in the second method, the resulting liquid boiled at 78—79°/10 mm.

iso*Propylidene Glycerol* 3 : 5-*Dinitrobenzoate* (IV).—A mixture of 11·6 g. of 3 : 5-dinitrobenzoyl chloride and 8·2 g. of dry quinoline was dissolved in 15·6 c.c. of chloroform, 6·7 g. of *iso*propylidene glycerol were slowly added with cooling, and the whole was kept for 2 days. The product was shaken successively with water, dilute sulphuric acid, sodium bicarbonate solution, and water, then dried over ignited sodium sulphate, and the solvent removed. The residual oil solidified on cooling, and crystallised from ligroin (b. p. 40—60°) –benzene in colourless needles (yield 80%), m. p. 85°, soluble in benzene, ether, or chloroform, and nearly insoluble in ligroin (Found: N, 8·6. $C_{13}H_{14}O_8N_2$ requires N, 8·6%).

Glycerol α-*Mono*-3 : 5-*dinitrobenzoate* (III).—(a) A mixture of equivalent quantities of monosodium glyceroxide and 3 : 5-dinitrobenzoyl chloride in ether was kept for 2 days and then heated under reflux. The suspended matter, which had little or no alkaline reaction, was filtered off, and the solvent evaporated. The residual oil, which solidified, crystallised from chloroform in colourless needles, m. p. 118°, soluble in alcohol, ether, or benzene; it also

crystallised easily from water (Found: N, 9·75. $C_{10}H_{10}O_8N_2$ requires N, 9·79%).

(b) A mixture of 5 g. of *iso*propylidene glycerol 3 : 5-dinitrobenzoate and 100 c.c. of *N*/2-hydrochloric acid was stirred and heated at 70—80° for 1 hour. The clear liquid was decanted, and deposited glycerol α-dinitrobenzoate on cooling. This, after being dried in a vacuum over sulphuric acid and crystallised from chloroform (yield 70%), melted at 118°, alone or mixed with a specimen prepared by method (a).

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KING'S COLLEGE, LONDON, W.C. 2. [*Received, August 7th*, 1925.]

CCCLXXX.—*The Formation and Growth of Silver Nuclei in the Decomposition of Silver Oxalate.*

By JAMES YOUNGER MACDONALD and CYRIL NORMAN HINSHELWOOD.

THIS paper contains first a description of a sensitive method for making direct measurements of the instantaneous rate of reaction in a chemical change where gas is evolved, and secondly an account of its application in the investigation of certain interesting phenomena relating to the thermal decomposition of silver oxalate.

The decomposition of solid substances frequently offers the appearance of being autocatalytic, the rate of change increasing as the reaction progresses. This is in many instances due simply to an increase in the surface of the solid during the course of the transformation (*Phil. Mag.*, 1920, **40**, 569), but it can also be due to the circumstance that the reaction is facilitated by the presence of nuclei of one of the products. To whichever cause the acceleration is due, the relation between the velocity of change and the amount of reaction which has already taken place is a very complicated one. The determination of this relation from measurements of the total change, x, which has taken place at any time, t, depends upon the drawing of tangents to curves of x and t, a procedure involving a large proportional error. The following method was therefore adopted for obtaining direct readings of the actual velocity at different times during the reaction.

The solid is allowed to decompose in a small bulb kept at constant temperature in a vapour bath. The bulb is connected with a

McLeod gauge and the gaseous products of the reaction are removed by a continuously running Gaede pump. The experiments must be made at temperatures where the rate of evolution of gas is not too great, so that the pump is able to maintain a fairly high vacuum in the apparatus. At intervals measurements of the rate of reaction are made by turning off the tap leading to the pump and raising the mercury in the McLeod gauge for a pressure reading. At the moment when the mercury cuts off the bulb of the gauge from communication with the decomposition vessel a stop-watch is started. The pressure reading is completed and the mercury lowered, communication with the decomposition vessel being once more established. At the end of a suitable time a second reading of the McLeod gauge is made, the watch being stopped at the moment when the mercury once more cuts off the gauge from the rest of the apparatus. In the actual experiments pressure increases of the order of 0·1 or 0·01 mm. were measured in periods of time varying from 45 seconds to 15 minutes in reactions lasting several hours or days. The readings, therefore, can be regarded as instantaneous. By the use of gauges of various degrees of sensitiveness in different experiments it is possible either to follow the reaction over its whole course or to make a more detailed study of the initial stages.

No investigation has previously been made of the mechanism of the decomposition of silver oxalate. It is usually assumed that the change takes place in accordance with the simple equation $C_2O_4Ag_2 = 2Ag + 2CO_2$. This was confirmed by an analysis of the residue, which was more than 99·8% silver, and of the gas, which was pure carbon dioxide containing no trace of carbon monoxide. If the reaction involved the intermediate formation of carbonate or oxide, carbon monoxide would necessarily appear in the gaseous products.

Various specimens of silver oxalate behaved very differently, falling roughly into two classes. One class decomposed with the most marked acceleration, the maximum velocity being about 200 times greater than the initial velocity. The other class showed very much less acceleration, and the velocity, instead of passing through a sharp maximum, remained steady over a large part of the whole course. Specimens of this second class were on the whole about ten times as stable as those of the first class. The difference was traced to one factor in the method of preparation. All the specimens were prepared by precipitation of silver nitrate with sodium oxalate. Those precipitated under such conditions that the sodium oxalate was in excess throughout belonged to the unstable accelerating type, whilst those precipitated with silver nitrate always in excess belonged to the stable, feebly accelerating type.

The method of preparation was carefully standardised. The precipitant which was not to be in excess was run slowly as a fine continuous stream in the course of about ½ hour into a solution of the other salt, which was vigorously agitated by a mechanical stirrer. All the solutions were very dilute—an obvious precaution in view of Richards' well-known investigation of the occlusion difficulties of Stas—and the precipitation was carried out in blackened vessels at the ordinary temperature. The silver oxalate was repeatedly washed by decantation, and dried in a vacuum desiccator kept in a dark cupboard. As far as we are able to judge, all factors were exactly the same in the preparation of the two types of silver oxalate except that one or other precipitant was in excess.

The autocatalytic acceleration is not due to carbon dioxide, since it takes place in a vacuum. It is not due simply to increase in surface, as with potassium permanganate and some other solids (*loc. cit.*), since it cannot be eliminated by preliminary grinding. It must be due, therefore, to nuclei of solid silver formed in the decomposition. Since the initial velocity is very small compared with that finally attained, the whole course of the reaction is evidently governed by the formation and growth of these nuclei. The decomposition of solids is essentially a surface phenomenon. Moreover, the devitrification of glass, which depends upon the formation of crystal nuclei, is known to start from the surface, since the washing of the surface with dilute hydrofluoric acid removes the tendency to further devitrification on heating. It is very probable that in a similar way the silver nuclei are formed at the surface of the oxalate crystals. The formation of nuclei and their subsequent growth are independent phenomena both of which are extremely sensitive to the presence of foreign substances (compare Zsigmondy, "Kolloidchemie," 1922, p. 144). When silver oxalate is precipitated with excess of silver nitrate and sodium oxalate, respectively, there will probably be different ions adsorbed. The different behaviour of the oxalate prepared by these two methods is to be attributed to the effect of the adsorbed ions on the chance of formation of silver nuclei in the solid and on their subsequent growth.

As the silver oxalate was always very thoroughly washed during preparation, only the definitely adsorbed ions need be taken into account.

The decomposition bulb was protected from light by a covering of tinfoil.

About fifty experiments were carried out with twelve specimens of oxalate. Some of the results are in the following tables and curves; t is the time in minutes, and v the velocity of reaction in arbitrary units.

Temperature 131·8°.

(*a*) Silver oxalate precipitated with excess of sodium oxalate.

t.	*v.*	*t.*	*v.*
5	5·3	39·5	756
12	60	43	628
18	147·5	49	434
21	216	53	340
25	384	60	192
28·5	725	75	154
30·5	958	96	46
32·5	850	140	28·5
35·5	888	263	13·3

This specimen was precipitated with a very large excess of oxalate, and is one of the most unstable.

(*b*) Silver oxalate precipitated with excess of silver nitrate.

t.	*v.*	*t.*	*v.*
3·5	7	240	48
10	13	270	50
33	32	305	48
43	28	335	31
47	33	360	24
60	31	420	18
105	50	540	13
150	43	600	6·3
180	43		

The rise and fall in velocity is quite real, and presumably connected with the fact that the oxalate grains are not quite uniform.

Using a more sensitive gauge it is possible to see in more detail the initial variations in rate. The following results were obtained with a rather more stable specimen of oxalate. Up to 100 minutes, the decomposition amounts to about 1% only. Temperature 131·6°.

t.	*v.*	*t.*	*v.*	*t.*	*v.*	*t.*	*v.*
5	3·4	32·5	45·8	77·5	224	135	477
12·5	3·9	37·5	62·8	86·5	255	149	516
17·5	5·8	47·5	107·2	97·5	310	165	549
22·5	15·6	58·5	152	110·5	374	198·5	580
27·5	26·8	67·5	183	121	407	204·5	618

In this experiment, the maximum rate of nearly 3000 was reached in about 6 hours.

It is worth while to give in full the results of one more experiment, made at 110° with a specimen of the accelerating type. Attention may be directed to the long period of steady velocity following the sharp fall from the maximum.

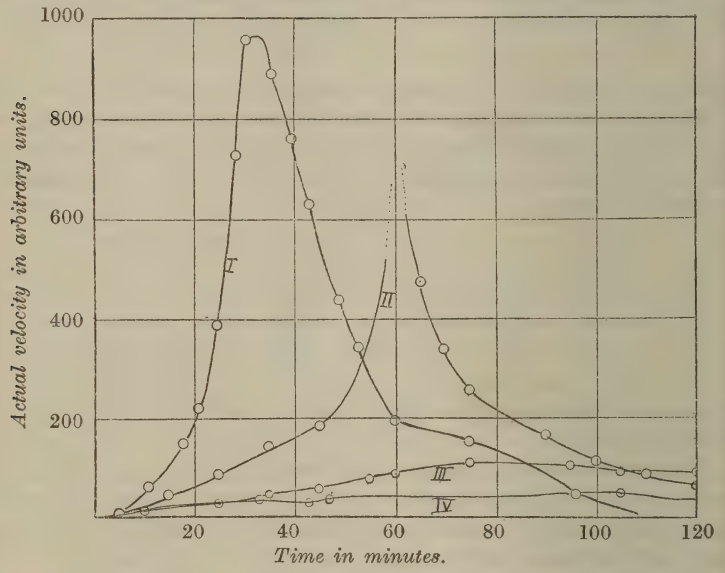
t.	*v.*	*t.*	*v.*	*t.*	*v.*
5	1·09	759	182	2,405	83·2
15	1·22	832	214·5	2,575	83·5
25	1·28	881	224·5	2,813	78·7
40	1·79	936	251	3,127	72·9
60	2·70	1,126	298	3,858	51·4
85	4·72	1,197	276	4,303	45·9
135	12·0	1,331	228	5,180	33·7
170	18·6	1,400	189·5	6,012	25·7
245	35·7	1,607	115	6,708	19·3
313	50·0	1,737	98·0	8,873	16·7
438	69·4	2,293	78·0	9,617	14·1
533	90·8	2,310	82·9	13,920	8·7
				19,700	5·6

The relation between the velocity and the amount decomposed is not by any means simple. G. N. Lewis, investigating the some-

what similar decomposition of silver oxide (*Z. physikal. Chem.*, 1905, **52**, 310), thought that the results could be expressed by the simple equation for homogeneous autocatalysis $dx/dt = kx(a - x)$. It is difficult to see how the complex process of nucleus formation and growth can be so represented. The applicability of the equation to the silver oxalate decomposition can be tested in two ways. (*a*) dx/dt is plotted against t and, by square counting, a curve of x and t is constructed. It is then readily seen by plotting $\log [dx/dt/(a - x)]$ against $\log x$ whether the rate per unit amount

FIG. 1.

Influence of the method of precipitation on the decomposition of silver oxalate.



Curves I and II: silver oxalate precipitated in presence of excess of sodium oxalate. Curves III and IV: excess of silver nitrate.

of oxalate is a linear function of x. It is not. The rate depends upon a power of x which not only varies but is always less than unity. (*b*) For the very early stages of the reaction, as measured with a more sensitive gauge, the equation reduces to $dx/dt = kx$, but to account for the fact that the reaction starts at all this has in any case to be written $dx/dt = k\ (x + x_0)$, where x_0 is a small constant quantity which determines the actual initial rate. From this it follows that $\log dx/dt = kt +$ constant. This gives a convenient means of plotting the results without resorting to the laborious process of square counting. The following table contains a set of typical results, the figures referring to the initial stages of

one of the experiments already quoted (second table). $dx/dt = v$. When $t = 5$, $\log v = 0{\cdot}53$.

$t - 5$.	$\log v - 0{\cdot}53$.	$\frac{\log v - 0{\cdot}53}{t - 5}$.	$t - 5$.	$\log v - 0{\cdot}53$.	$\frac{\log v - 0{\cdot}53}{t - 5}$.
12·5	0·23	0·0184	53·5	1·652	0·0309
17·5	0·663	0·0379	62·5	1·713	0·0274
22·5	0·898	0·0399	72·5	1·820	0·0251
27·5	1·131	0·0412	81·5	1·877	0·0230
32·5	1·268	0·0390	92·5	1·961	0·0212
42·5	1·500	0·0353	105·5	2·043	0·0194

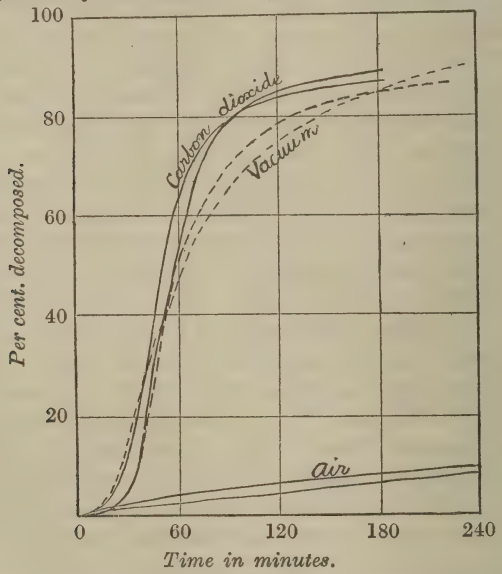
Influence of Adsorbed Gases on the Silver Nuclei.—Some experiments were also made in which the silver oxalate was allowed to decompose in a small bulb connected with a gas burette, the rate of reaction being measured simply by the total evolution of carbon dioxide. The results were most unexpected. Sometimes there was no trace of acceleration, even with specimens prepared by precipitation with excess of sodium oxalate. At other times the acceleration made its appearance after varying intervals of time in an uncontrollable manner. This was all traced to the influence of the air initially present in the bulb. Further investigation showed that oxygen has a pronounced poisoning influence on the reaction. This is evidently due to its being adsorbed on the nuclei of silver as soon as they are formed on the surface. Their growth is thus hindered or stopped. Experiments carried out in an atmosphere of carbon dioxide followed almost exactly the same course as those carried out in a vacuum and the influence of nitrogen appears to be but slight. Fig. 2 shows clearly the pronounced poisoning influence of air. The explanation is now obvious of the puzzling results obtained when silver oxalate is allowed to decompose in a bulb initially filled with air which is gradually replaced by carbon dioxide; there is a sudden acceleration of the reaction when the air is all displaced from the surface of the crystals. In order to study the reaction under conditions where the poisoning effect of air was constant, experiments were made in a stream of air, the rate of reaction being measured periodically by cutting off the stream and allowing the pressure to rise. The stream was sufficiently slow for there to be no appreciable cooling effect, as the air passed through a considerable length of heated tubing before actually coming into contact with the silver oxalate. In a continuous stream of air, or even in the presence of still air the reaction is spread out over a time about ten times as long as in a vacuum or in presence of carbon dioxide. The poisoning effect is relatively more marked with the unstable accelerating specimens precipitated with excess of sodium oxalate than with those precipitated in presence of an excess of silver

nitrate, since in the latter the acceleration is already to some extent inhibited.

The changes in colour which accompany the decomposition are interesting, the white oxalate passing through pale to deep brown and then becoming black. When the reaction is nearly complete some sort of recrystallisation of the silver seems to occur and the whole mass becomes almost white. Addition of the final product does not cause an increase in the rate of reaction. Evidently coarser particles of silver are not effective in catalysing the change in the same way as the minute nuclei formed in the space lattice of

FIG. 2.

Influence of air on the decomposition of silver oxalate.



the oxalate crystals themselves. Experiments were made on the influence of previous grinding. This produced some increase in the rate of reaction, but did not eliminate the autocatalysis as with potassium permanganate and some other solids.

The influence of temperature was investigated with a few of the specimens. It is normal, and more or less uniform throughout all stages of the decomposition. Over the range 100° to 150° the rate increases approximately 2·7 times for 10°.

Summary.

The thermal decomposition of silver oxalate takes place in accordance with the simple equation $(CO{\cdot}OAg)_2 = 2Ag + 2CO_2$.

Its rate is governed entirely by the formation and growth of nuclei of silver in the space lattice of the oxalate crystals.

These processes are sensitive to the presence of adsorbed ions, since silver oxalate precipitated in presence of excess of sodium oxalate behaves quite differently from that precipitated in presence of excess of silver nitrate. This is in some respects analogous to the influence of adsorbed ions on the photo-sensitivity of silver bromide described by Fajans and Frankenburger (*Z. Elektrochem.*, 1922, **28**, 499).

In a vacuum and in an atmosphere of carbon dioxide the rate of reaction is the same, but the presence of oxygen has a very pronounced poisoning effect on the silver nuclei. This is an example of catalytic poisoning of a new kind. The influence of adsorbed ions and of oxygen seems to show that the nuclei must be first formed at the surface of the oxalate crystals, rather than at any point in the interior.

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CCCLXXXI.—*The Influence of Different Nuclei on the Absorption Spectra of Substances.*

By JOHN EDWARD PURVIS.

IN previous papers (J., 1914, **105**, 590, 1372) the author described the absorption spectra of substances containing several benzene nuclei, and it was shown that the phenomena were very different in substances containing two, three, and four benzene residues even when the nuclei with which they were combined had no specific absorption.

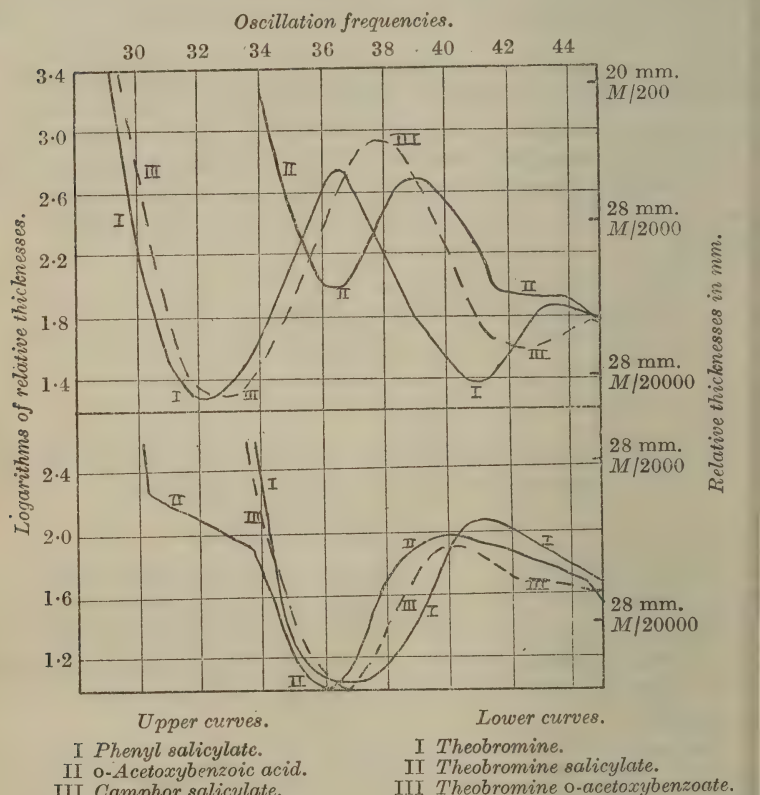
The aim of this communication is to describe the absorption spectra in the ultra-violet region (1) of substances in which each nucleus shows specific absorption when uncombined, and (2) of substances in which only one of the nuclei shows specific absorption.

Alcoholic solutions of the following substances were examined: Salicylic acid, phenyl salicylate, *o*-acetoxybenzoic acid, benzyl salicylate, thymol salicylate, camphor, camphor salicylate, theobromine, theobromine salicylate, theobromine *o*-acetoxybenzoate, caffeine, caffeine salicylate, caffeine benzoate, caffeine citrate, caffeine hydrochloride, phenazone, phenazone salicylate, quinine, quinine salicylate, and quinine *o*-acetoxybenzoate. Most of the substances were examined in the first instance in *M*/200-solution,

but theobromine and caffeine and their salicylates were soluble only in about $M/2{,}000$-strength. A condensed cadmium spark was the source of radiant energy.

Salicylic acid. Hartley's observation (J., 1888, **53**, 641) that this substance has two bands in the ultra-violet region has been confirmed.

FIG. 1.



Phenyl salicylate. This has two bands like those of the acid. On comparing photographs of the two substances it was clear that there was a shift towards the red end and the less refrangible band of the salt was not so strong as that of the acid; and also the more refrangible band was better marked. Fig. 1, I (upper series) gives the curve for the salt.

o-*Acetoxybenzoic acid.* The replacement of the hydrogen in the hydroxyl group by acetyl has produced a striking change in the absorption (Fig. 1, II, upper series). The less refrangible band at

1/λ3650 (λ2740) is much weaker and is shifted towards the more refrangible regions. When the spectrum is compared with that of salicylic acid or phenyl salicylate, the more refrangible band is represented by an extension of the rays from 1/λ4150 (λ2408) to 1/λ4350 (λ2298). The general appearance of the absorption is not unlike that of benzoic acid and this is usually assigned to the benzene nucleus.

Thymol salicylate. Benzyl salicylate. The bands of these two substances were similar to those of salicylic acid and phenyl salicylate, and differed chiefly in position, corresponding to differences in their respective molecular weights. The three benzene bands of the benzyl nucleus do not appear as they do in such substances as dibenzyl carbamate and benzyl chloride (Purvis, J., 1914, **105**, 1372; 1915, **107**, 496). The curves have not been reproduced.

Camphor salicylate. The curve (Fig. 1, III, upper series) shows that the two bands of the acid have not been very much affected. The differences are that the less refrangible band is not so strong as that of salicylic acid or of phenyl salicylate, and the more refrangible band is weaker. Camphor has a weak band at 1/λ3480 (λ2870) as described by Baly, Marsden, and Stewart (J., 1906, **89**, 979) and confirmed by Hartley (J., 1908, **93**, 961) and by the author (J., 1915, **107**, 643).

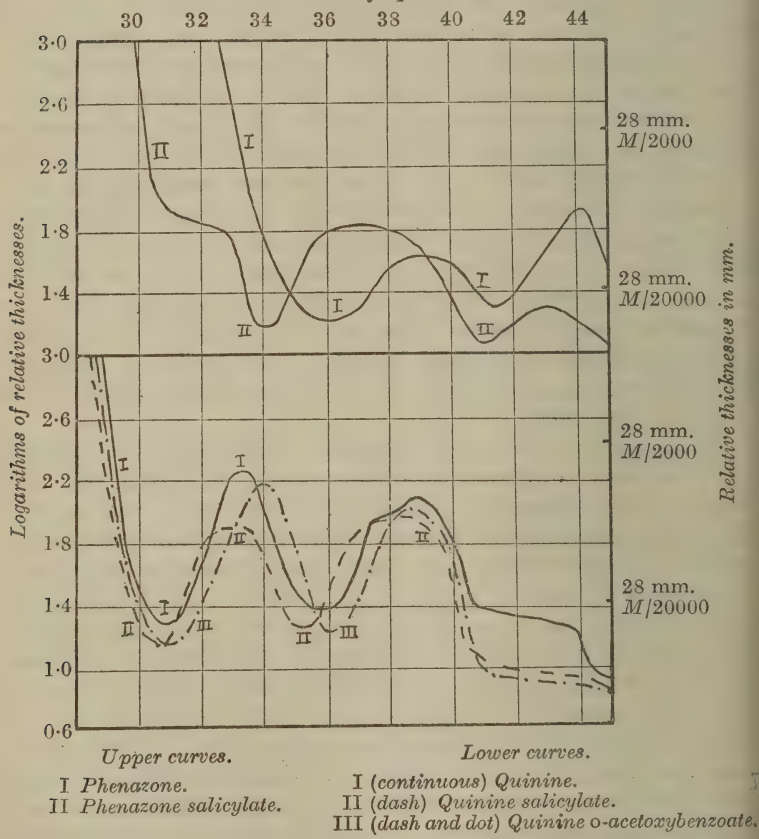
Theobromine; theobromine salicylate; theobromine o-*acetoxybenzoate. Caffeine; caffeine salicylate.* Hartley (J., 1905, **87**, 1796) describes the absorption spectra of theobromine and caffeine. His photographs show a definite band in theobromine but not in caffeine. In the text he states that "there is a sudden lengthening of the spectrum and its enfeeblement between 1/λ3675 (λ2720) and 1/λ3794 (λ2635), as if an absorption band was indicated hereabouts of a very feeble or ill-defined character." The author has repeated the observations and finds that caffeine has a definite band like that of theobromine, but shifted a little more towards the red end. The curves of theobromine and its salts (Fig. 1, I, lower series) show that the rays passing through theobromine salicylate rapidly step out between 1/λ3030 (λ3298) and 1/λ3350 (λ2980), and there is a band at 1/λ3650 (λ2740). It is obvious from this that the acid nucleus exerts some influence on the absorption. The curve of theobromine *o*-acetoxybenzoate shows considerable differences. It is not unlike that of theobromine itself but narrower, and the ultimate effect is comparable with that of salicylic acid and *o*-acetoxybenzoic acid described above.

Solutions of caffeine and caffeine salicylate show similar phenomena to theobromine and theobromine salicylate.

Caffeine benzoate: caffeine citrate: caffeine hydrochloride. Solu-

tions of these salts give results like those of the base itself, except in regard to the positions of the bands, which vary according to the molecular weights. The author (J., 1915, **107**, 966) showed that benzoic acid has a weak band at 1/λ3600 (λ2770), and also that there was a rapid step-out of the rays from about λ2320 into the

FIG. 2.



Schumann region. Hartley and Hedley earlier (J., 1909, **91**, 314) had indicated the presence of the weak band only. It is clear, therefore, that the acid nucleus has not affected the general form of the caffeine absorption. Neither citric acid nor hydrochloric acid gives specific absorption in these ultra-violet regions. The curves have not been reproduced.

Phenazone; phenazone salicylate. The curve shows (Fig. 2, upper curves) that phenazone has two wide bands at 1/λ3600 (λ2776)

and 1/λ4150 (λ2409). The salt shows a rapid extension of the rays between 1/λ3050 (λ3270) and 1/λ3260 (λ3066), and two weak bands at 1/λ3400 (λ2940) and 1/λ4100 (λ2438). As in theobromine and caffeine, the rapid extension of the rays may mean the remnant of the less refrangible band of salicylic acid.

Quinine, quinine salicylate, quinine o-*acetoxybenzoate.* Hartley (*Phil. Trans.*, 1885, **176**, 471) first described two bands in solutions of quinine at about 1/λ3100 (λ3225) and 1/λ3600 (λ2770). Dobbie, Lauder, and Fox (J., 1911, **99**, 1254; 1912, **101**, 77) described a third weak band at 1/λ3740 (λ2670). The author has repeated these experiments and finds only a very weak indication of this third band. The curves (Fig. 2, lower curves) show that the original quinine bands have suffered some changes in strength and position in the salicylate. Both the bands of the salicylate are weaker than those of the base. In the case of the *o*-acetoxybenzoate there is a return to phenomena not unlike those of the base itself, and there is a shift back nearer to the latter. These changes are comparable (although the differences are not so great) with those of salicylic acid and *o*-acetoxybenzoic acid and of theobromine and its salts described above. The rapid extension of the rays from 1/λ4100 is noticeable in all three substances.

Results.—The chief results of these observations are: (1) the bands of phenyl, benzyl, thymol, and camphor salicylates are comparable with those of salicylic acid: the differences from the latter, and from one another, being chiefly in position and strength; (2) the basic nucleus is the chief agent in the specific absorption of the benzoate, citrate and hydrochloride of caffeine; (3) in the salicylates of theobromine, caffeine, phenazone and quinine, the acid nucleus modifies that of the basic nucleus to a larger extent, but least in the quinine compound: (4) in *o*-acetoxybenzoic acid, and in the *o*-acetoxybenzoates of theobromine and quinine the replacement of the hydrogen of the hydroxyl group by the acetyl group exerts a very great influence on the final absorption.

It is clear, therefore, that the specific and the general absorption of these substances depend upon three factors; (*a*) the nature of the base, (*b*) the nature of the acid, and (*c*) the presence of hydrogen in the hydroxyl group. Now benzoic acid has a very weak band at 1/λ3600 (λ2777) and phenol a very strong one at 1/λ3670 (λ2720). The carboxyl group in the one and the hydroxyl group in the other destroy the well-known bands of benzene: and the hydroxyl group replaces these by a much stronger one than is produced by the carboxyl group. It appears from these experiments that the replacement of the hydrogen atom of the hydroxyl group by another radical, not itself possessing any specific absorption, decreases the

absorption capacity of the other parts of the molecule: or, to put it another way, the vibration of this hydrogen atom is a very powerful factor in the absorption.

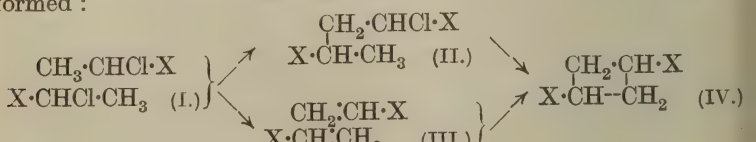
PUBLIC HEALTH CHEMICAL LABORATORY,
CAMBRIDGE. [*Received, September 14th*, 1925.]

CCCLXXXII.—*The Possible Enhanced Activity of Newly-formed Molecules.*

By FRANK ROBERT GOSS and CHRISTOPHER KELK INGOLD.

IN the course of investigations carried out during the past few years, the authors have frequently been unable to confirm an apparently obvious reaction mechanism by preparing the supposed intermediate products and subjecting them to the conditions of the original experiment; the substances either remained unaltered or behaved differently from expectation. Similar experiences have been recorded by others, and the phenomenon appears sufficiently widespread to give some support for the suggestion that intermediates may be produced in a reactive condition in which they are capable of changes which cannot occur after the energy associated with the formation of the compound has been dissipated. This hypothesis of "nascent molecules" is, of course, not new; but it is one which should be accepted only after conclusive evidence has been furnished, and whilst it is not claimed that the observations recorded in this paper constitute sufficient grounds for embracing so far-reaching a hypothesis, they appear to possess some significance from this point of view.

Two mechanisms suggest themselves for the formation of the *cyclo*butane ester (IV) (Markovnikov and Krestovnikov, *Annalen*, 1880, **208**, 334) from α-chloropropionic ester (I) and sodium ethoxide: the elimination of hydrogen chloride is either inter-molecular, in which case γ-chloro-α-methylglutaric ester (II) is the intermediate product, or intramolecular, ethyl acrylate (III) being first formed:



The chloro-ester (II) has been prepared and subjected to the action of sodium ethoxide under the same conditions. It gave no

detectable quantity of the *cyclo*butane ester, but, on the other hand, yielded the *cyclo*propane ester (V), together with the lactonic ester (VI), the unsaturated ester (VII) and the ethoxy-ester (VIII).

(V.) $H_2C<\begin{matrix}CH\cdot CO_2Et\\ |\\ C(CH_3)\cdot CO_2Et\end{matrix}$ $H_2C<\begin{matrix}CH(CO_2Et)\cdot O\\ |\\ CH(CH_3)--CO\end{matrix}$ (VI.)

$CO_2Et\cdot CHMe\cdot CH{:}CH\cdot CO_2Et$ (VII.) $CO_2Et\cdot CHMe\cdot CH_2\cdot CH(OEt)\cdot CO_2Et$ (VIII.)

Acrylic ester (III) was treated in a similar manner. Again no *cyclo*butane ester could be detected, but only its unsaturated isomeride, α-methyleneglutaric ester (IX), which was the chief product apart from β-ethoxypropionic ester (X).

(IX.) $CO_2Et\cdot CH_2\cdot CH_2\cdot C(:CH_2)\cdot CO_2Et$ $EtO\cdot CH_2\cdot CH_2\cdot CO_2Et$ (X.)

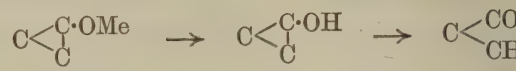
Although these experiments provide no direct evidence of the intervention either of (II) or of (III) in the series of changes leading to the *cyclo*butane ester (IV), it may not be inappropriate to suggest that if the later change depends on the energy of formation of the intermediate, probably it is acrylic ester that acts in this way; for not only are four-membered rings produced on the whole more easily by additive synthesis than by the closure of a chain, but also the double linking in acrylic ester is more likely to derive temporary activity from its own formation than are the chlorine or methyl-hydrogen atoms of (II) from a reaction in which they are not directly concerned. In this connexion, the suggestion may tentatively be advanced that the double bond in acrylic ester is possibly semi-polar when first produced (which it would be if hydrogen and chlorine were removed from chloropropionic ester, not as atoms, but as ions), although it is undoubtedly non-polar in the ordinary substance (Sugden, Reed, and Wilkins, this vol., p. 1525).

It has been observed (J., 1922, **121**, 1552) that α-campholenic acid (XI) when warmed with an alkaline suspension of silver oxide becomes partly converted into camphor (XIII), and the suggestion was advanced that reduction to dihydrocampholenic acid (XII) first occurred. This reaction has again been investigated and both *cis*- and *trans*-dihydrocampholenic acids have been subjected to similar experimental conditions; both, however, remained unaltered.

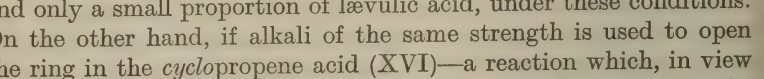
$$\underset{\text{(XI.)}}{C_8H_{13}\cdot CH_2\cdot CO_2H} \longrightarrow \underset{\text{(XII.)}}{C_8H_{15}\cdot CH_2\cdot CO_2H} \longrightarrow \underset{\text{(XIII.)}}{C_8H_{14}<\begin{matrix}CO\\ |\\ CH_2\end{matrix}}$$

Other cases have been observed in connexion with the opening of the *cyclo*propanol ring. It has been shown that methoxy-

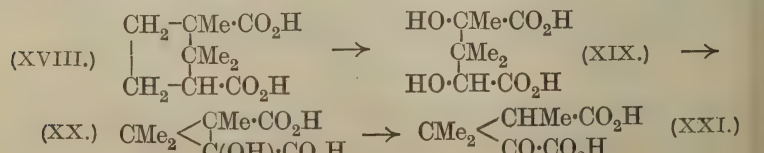
*cyclo*propanes on treatment with demethylating agents yield first *cyclo*propanols, which may undergo further conversion into open-chain ketones, the extent of the latter reaction being limited by its reversibility and the consequent equilibrium, which varies from case to case:



In the case of the methoxy-ring acid (XIV), the corresponding keto-acid is, of course, acetosuccinic acid (XV), which, if acid is used as demethylating agent, passes into lævulic acid with loss of carbon dioxide. It is more remarkable, however, that when concentrated alkali is employed, lævulic acid is still the sole product, although acetosuccinic esters yield mainly succinic and acetic acids, and only a small proportion of lævulic acid, under these conditions. On the other hand, if alkali of the same strength is used to open the ring in the *cyclo*propene acid (XVI)—a reaction which, in view of the known tendency of glutaconic acids to add on water in the presence of alkalis, giving β-hydroxy-acids (*e.g.*, XVII), can scarcely be supposed to proceed otherwise than through acetosuccinic acid—only succinic and acetic acids are produced.



Whilst the mechanism formulated below has been established as the most probable one for the formation of Balbiano's acid (XXI) from camphoric acid (XVIII) by oxidation, Pandya and Thorpe (J., 1923, **123**, 2858) synthesised the intermediate hydroxy-ring acid (XX) but could not convert it into Balbiano's acid. Although working with other ends in view, they were struck by this and suggested that the real intermediary was the opposite stereoisomeride to that which they had synthesised; it can, however, readily be seen from models that the intervening hydroxy-acid should possess precisely the configuration of the acid which Pandya and Thorpe synthesised and found unreactive. Other similar instances involving the failure of a ring to open have been recorded from time to time and some of these are now under investigation.



Experimental.

Action of Sodium Ethoxide on Ethyl α-Chloropropionate.—Ethyl α-chloropropionate, prepared from pure, dry lactic acid (Brühl, *Ber.*, 1876, **9**, 35), was treated with sodium ethoxide as described by Markovnikov and Krestovnikov (*loc. cit.*) and by Haworth and Perkin (J., 1898, **73**, 336). To 20 g. of the ester at 80°, dry sodium ethoxide (10 g.) was added in small portions; the temperature was finally kept at 100° for 3 minutes, and after cooling the product was poured into dilute acid and isolated by extraction with ether. As stated by Markovnikov and Krestovnikov, it consisted mainly of ethyl α-ethoxypropionate, b. p. 50°/4 mm. This was converted into its amide, which melted at 63° after crystallisation from petrol (b. p. 40—60°) and was identified with that described by Wurtz (*Ann. chim.*, 1860, **59**, 174) (Found: C, 50·9; H, 10·0. Calc., C, 51·2; H, 9·5%). The remainder (about 10%) of the product, b. p. 120°/4 mm., consisted of the *cyclo*butane-1 : 3-dicarboxylic ester, which was converted by hydrolysis into the corresponding acid, m. p. 170°, as described by Markovnikov and Krestovnikov.

Action of Sodium Ethoxide on Ethyl α-Chloro-γ-methylglutarate.—Ethyl α-chloro-γ-methylglutarate (this vol., p. 393) was prepared by treating the lactone of ethyl α-hydroxy-γ-methylglutarate with phosphorus pentachloride and pouring into alcohol. The decomposition with sodium ethoxide (12 g. and 40 g. of the ester) was carried out as described above, and the product was completely hydrolysed. The acids were digested for some days with an aqueous suspension of precipitated calcium carbonate, and the filtered solution was concentrated and allowed to crystallise; the calcium salt of the *trans-cyclo*propane acid (m. p. 168°) then separated. The filtrate from the calcium salts was worked up for organic acids, which were converted through their silver salts into benzyl esters. The portion of these boiling below 240°/15 mm. yielded the original lactone on hydrolysis. By distillation at 1 mm. the less volatile esters were separated into a small preliminary fraction from which on hydrolysis α-methylglutaconic acid together with a liquid acid (probably the ethoxy-acid described below) was obtained, and a fraction (32 g.), b. p. 230—260°, which on hydrolysis gave a liquid consisting, as analysis indicated, mainly of the ethoxy-acid. This was purified by careful distillation of the *ethyl* ester, b. p. 126—129°/12—14 mm. (Found: C, 58·1; H, 9·0. $C_{12}H_{22}O_5$ requires C, 58·5; H, 8·9%); the liquid *acid* was recovered by hydrolysis (Found: C, 50·2; H, 7·5. $C_8H_{14}O_5$ requires C, 50·5; H, 7·3%).

Action of Sodium Ethoxide on Ethyl Acrylate.—Ethyl acrylate was prepared from ethyl αβ-dibromopropionate by Röhm's method

(*Ber.*, 1901, **34**, 573). The reaction was carried out exactly as described in the case of ethyl α-chloropropionate, except that for 20 g. of ester 15 g. of sodium ethoxide were employed. The products were isolated in an identical manner and again consisted to the extent of nine-tenths of a liquid distilling at 50°/4 mm. and one-tenth of a liquid distilling at 120°/4 mm. The former was shown to be ethyl β-ethoxypropionate (compare Purdie and Marshall, J., 1891, **59**, 475) by conversion into the corresponding amide described by Kilpi (*Z. physikal. Chem.*, 1912, **80**, 184), which was crystallised from water; m. p. 50° (Found: C, 50·6; H, 10·1. Calc. for $C_5H_{11}O_2N$, C, 51·2; H, 9·5%). The high-boiling fraction consisted of ethyl α-methyleneglutarate and yielded on hydrolysis the corresponding acid, m. p. 130° (Röhm, *Ber.*, 1901, **34**, 427).

α-Campholenic Acid and α-Campholenamide.—*dl*-Campholenonitrile, b. p. 100°/5 mm., was prepared by the method of Tiemann (*Ber.*, 1895, **28**, 2167) from *d*-camphoroxime, and obtained in 75% yield. It was converted into a mixture of the acid and amide by boiling 3 g. with a solution of 5 g. of potassium hydroxide in 25 c.c. of ethyl alcohol. Addition of water precipitated the amide, m. p. 122°, and more was obtained by extracting the filtrate. The acid extracted after acidification of the mother-liquor distilled at 137°/1 mm.

α-Campholanic Acid.—The *cis*-acid was prepared by the reduction of α-campholenic acid with hydrogen and platinum black (Lipp, *Ber.*, 1922, **55**, 1883). It was distilled at 140°/1 mm.

The *trans*-acid was obtained by reducing α-campholenamide in the same way (*loc. cit.*) and hydrolysing the α-campholanamide first formed by boiling for 50 hours with 3 g. of potassium hydroxide in 15 c.c. of alcohol. The acid was distilled at 141°/1 mm.

Action of Silver Oxide on α-Campholenic Acid and α-Campholanic Acid.—α-Campholenic acid and *cis*- and *trans*-α-campholanic acids were added in separate experiments to a suspension of 2·5 g. of silver oxide in a solution of 0·5 g. of calcium oxide in 25 c.c. of water. In the experiment with α-campholenic acid, the silver oxide was rapidly reduced and the amount of camphor deposited in the condenser reached a maximum after 4 hours' heating. The saturated acids, however, gave no trace of camphor under similar conditions even after several days, and the silver oxide remained apparently unaltered.

Action of Hydrochloric Acid on 3-Methoxy-3-methylcyclopropane-1:2-dicarboxylic Acid.—The acid, prepared as described by Goss, Ingold, and Thorpe (J., 1923, **123**, 3358; this vol., p. 468), was boiled for 2 hours with ten times its weight of 20% hydrochloric acid. From the product a quantitative yield of lævulic acid was

obtained, which was identified by direct comparison and through its semicarbazone and phenylhydrazone, the m. p.'s of which were not depressed by admixture with genuine specimens of the respective substances. The lactone of 3-hydroxy-3-methyl*cyclo*propane-1 : 2-dicarboxylic acid was unaffected by this treatment.

Action of Potassium Hydroxide on 3-*Methoxy*-3-*methyl*cyclo*propane*-1 : 2-*dicarboxylic Acid.*—The acid was boiled for 30 minutes with 64% aqueous potassium hydroxide. From the cooled solution ether extracted lævulic acid, which was identified as described above. The lactone of 3-hydroxy-3-methyl*cyclo*propane-1 : 2-dicarboxylic acid was unaffected by the same treatment.

Action of Hydrobromic Acid on the Methoxy-acid : Formation of 3-*Methyl*-Δ^2-cyclo*propene*-1 : 2-*dicarboxylic Acid.*—The methoxy-acid was boiled for 1 hour with 20 parts by weight of concentrated hydrobromic acid, and the resulting solution was diluted and extracted with ether, methyl*cyclo*propenedicarboxylic acid being obtained.

Action of Potassium Hydroxide on 3-*Methyl*-Δ^2-cyclo*propene*-1 : 2-*dicarboxylic Acid.*—(1) The ring-acid was boiled for 2 minutes with 55% aqueous potassium hydroxide, and the solution was cooled, strongly acidified, and extracted with ether. Unchanged material was recovered.

(2) The experiment was repeated, the time being increased to 30 minutes. The product consisted of a mixture of the *cyclo*propene acid and succinic acid, which were separated by fractional crystallisation and identified by direct comparison.

(3) The ring-acid was boiled for 2 minutes with 64% potassium hydroxide. On working up for acids, a mixture of the *cyclo*propene acid and succinic acid was obtained.

(4) The above experiment was repeated, the time being increased to 30 minutes. The solid product consisted solely of succinic acid. Acetic acid also was produced, but this was detected by qualitative tests only and was not purified.

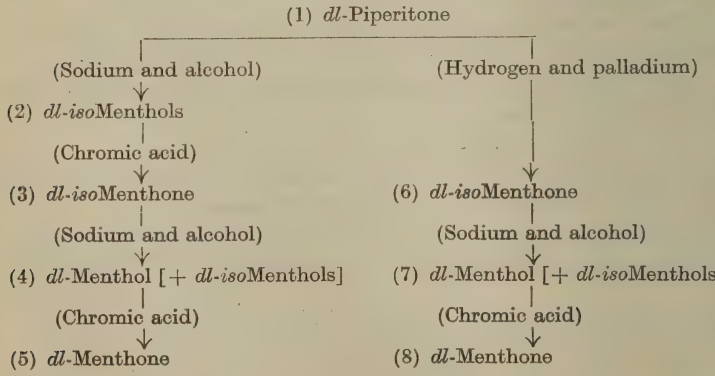
We desire to thank the Chemical Society for a grant which has defrayed part of the expense of this investigation.

THE UNIVERSITY, LEEDS. [*Received, May* 21*st*, 1925.]

CCCLXXXIII.—*Researches in the Menthone Series. Part I.*

By John Read and Alison Mary Ritchie Cook.

The information hitherto available respecting *dl*-menthone is derived mainly from the work of Pickard and Littlebury on the catalytic reduction of thymol (J., 1912, **101**, 109) and a note by Wallach on the catalytic reduction of synthetic *dl*-Δ^1-*p*-menthen-3-one (*Annalen*, 1913, **397**, 217). It is questionable whether a pure specimen of *dl-iso*menthone had been prepared and recognised as such prior to the work of Hughesdon, Read, and Smith on the reduction of piperitone (J., 1923, **123**, 2916). The "inactive menthone" prepared by Wallach gave the semicarbazone (m. p. 212°) characteristic of *dl-iso*menthone, whilst the derived oxime (m. p. 79—80°) corresponded with *dl*-menthone. These and other apparent inconsistencies in the literature of the subject have now been satisfactorily explained, and it has been found possible to convert *dl*-piperitone at will into derivatives of either series. Alkaline reduction of *dl*-piperitone (1, below) yields a mixture of liquid and solid menthols, in which it has not proved possible to detect *dl*-menthol or *dl-neo*menthol; a preliminary examination of the menthols concerned indicates that they are derived from *dl-iso*menthone rather than from *dl*-menthone. By means of the operations summarised below, this material was transformed successively to *dl-iso*menthone (3), *dl*-menthol (4), and *dl*-menthone (5). In a further series of operations (6, 7, and 8) a more direct passage from *dl*-piperitone to *dl-iso*menthone and *dl*-menthone was secured:



The relationships may be explained on the basis of the establishment of definite dynamic equilibria between *iso*menthone and

menthone in the presence of alkali and under other influences. The main product of the alkaline reduction of *dl-iso*menthone is *dl*-menthol, which may be separated to a large extent in the crystalline form from the associated liquid material. The latter is probably composed largely of *dl*-menthol, accompanied by a liquid mixture of *dl-iso*menthols. From the above considerations it is clear that by repeated oxidation and reduction this liquid by-product may be used as a source of further quantities of crystalline *dl*-menthol. When *dl*-menthol is oxidised by chromic acid in the final operation it yields practically pure *dl*-menthone, which shows little tendency to isomerise into *dl-iso*menthone in the presence of this reagent. By treating the resulting *dl*-menthone with alcoholic alkali, however, it may be transformed into the equilibrium mixture of *dl*-menthone and *dl-iso*menthone. Through the careful avoidance of disturbances due to the use of alkaline reagents it has been possible to prepare a number of pure derivatives of *dl*-menthone and *dl-iso*menthone, the melting points of which are indicated in the following summary :

Derivative.	*dl-iso*Menthone.	*dl*-Menthone.	Wallach's value.
Oxime	99—100°	81—82°	79—80°
Benzoyloxime	55·5	72—73	69—70
*iso*Oxime	94—95	114—115	87—88
Semicarbazone (α)	225	185—186	219
„ (β)	177—178	161	—

The melting points of the semicarbazones of *dl-iso*menthone were observed by Hughesdon, Smith, and Read (*loc. cit.*). The values quoted in the last column suggest that the "inactive menthone" described by Wallach (*loc. cit.*) consisted of *dl-iso*menthone, from which the oxime was prepared in an alkaline medium. *dl-iso*-Menthoneoxime is remarkable by reason of its capacity for forming well-developed crystals, so that for the first time it becomes possible to submit a menthoneoxime to a complete goniometric examination. *dl*-Menthone and *dl-iso*menthone may most readily be discriminated by preparing the oximes or semicarbazones in weakly acid solutions.

Up to the present, attempts to reduce piperitone to menthol or menthone in an acid medium have been unsuccessful, the ketone being practically unaltered by such reagents as tin and concentrated hydrochloric acid or zinc dust and glacial acetic acid. Distinct evidence was obtained of the formation of an appreciable amount of *dl*-α-phellandrene during the alkaline reduction of *dl*-piperitone, the relationship being of particular interest in view of the occurrence together of the lævo-modifications of these two substances in various eucalyptus oils.

Experimental.

Products obtained through an Initial Alkaline Reduction of dl-*Piperitone.*—1. The piperitone used throughout this work was extracted from the essential oil of *Eucalyptus dives*, using sodium bisulphite (*J. Soc. Chem. Ind.*, 1923, **42**, 339T).

2. In order to avoid all possibility of the formation of optically active products, the piperitone (40 g.) was racemised by means of alcoholic sodium ethoxide, prior to reduction with sodium and alcohol (J., 1923, **123**, 2270, 2918). Altogether, 880 g. of *dl*-piperitone yielded 820 g. of crude menthol, which was submitted to two systematic distillations under diminished pressure. The first fraction (b. p. to 87°/10 mm.) had an odour similar to that of α-phellandrene: its physical characteristics (J., 1923, **123**, 1660), together with the ready formation of a nitrosite melting at 106—107° and resembling that of *dl*-α-phellandrene, indicated that the fraction consisted essentially of this terpene. A further series of reductions carried out with piperitone which had been carefully freed from phellandrene by two successive fractional distillations under diminished pressure gave a crude product (223 g.) containing 9·1% of a similar fraction with the following physical characteristics: b. p. to 87°/10 mm., $\alpha_D^{16°}$ −1·58° (1-dcm. tube), $n_D^{15°}$ 1·4798. It therefore appears conclusive that *dl*-α-phellandrene is formed to an appreciable extent in the alkaline reduction of *dl*-piperitone. The total yield of menthols was 42·4%.

3. Upon oxidation with chromic acid (*Annalen*, 1889, **250**, 325), a total quantity of 410 g. of the liquid product (b. p. 95—97°/10 mm.) yielded 332 g. of a liquid possessing the characteristic odour of menthone. When distilled twice under diminished pressure, 37% of the product distilled up to 82°/8 mm. ($\alpha_D^{17°}$ −0·18°, $n_D^{17°}$ 1·4553), and 40% at 82—85°/8 mm. ($\alpha_D^{17°}$ −0·34°, $n_D^{17°}$ 1·4571). The latter fraction was used in preparing the derivatives described below, and appeared to consist essentially of *dl-iso*menthone.

4. Upon reduction with sodium and alcohol in the usual manner, a specimen of the *dl-iso*menthone just described (24·7 g.) yielded a product (24·0 g.) which distilled almost completely at 100—105°/15 mm. Three distinct fractions, each boiling over a range of one degree between 102° and 105°/15 mm. and having $n_D^{16°} = 1·4640$, deposited crystalline material on cooling, the liquid becoming permeated in each instance with fine radiating needles reaching a length of 2 cm. When separated and dried on porous plate, the three specimens melted at 32—34° and yielded the characteristic *dl*-menthyl hydrogen phthalate.

5. The menthone obtained by oxidising the crystalline *dl*-menthol

from the preceding operation resembled the product described under (8) below, and thus consisted essentially of *dl*-menthone.

Products obtained through an Initial Catalytic Reduction of dl-*Piperitone*.—6. Carefully purified *dl*-piperitone (50 g.) was hydrogenated at the ordinary temperature, under a pressure of 0·25 atmosphere, in presence of colloidal palladium (J., 1923, **123**, 2921). The mixed yields from four operations, when systematically distilled under diminished pressure, gave a main fraction, b. p. 90—93°/18 mm., $n_D^{18°}$ 1·4580; this was optically inactive and appeared to be practically identical with product (3), thus consisting of *dl-iso*menthone.

7. Upon reducing 18 g. of the preceding product with sodium and alcohol, a yield of 15·5 g. of crude menthol was obtained. This failed to crystallise, but when fractionally distilled the portion passing over at 107—112°/23 mm. (9·3 g.) furnished 2·3 g. of crystals, which possessed the pronounced odour of ordinary menthol and melted at 32—34°. Not only these crystals but also a liquid fraction of somewhat lower boiling point (105—107°/23 mm.; $n_D^{16°}$ 1·4686) yielded the characteristic *dl*-menthyl hydrogen phthalate (Pickard and Littlebury, *loc. cit.*).

8. *dl*-Menthol (m. p. 32—34°; 54 g.) was oxidised with chromic acid in the usual manner, except that the temperature was raised to 70° in order to decompose the black, crystalline chromium compound. The crude product (45·1 g.), when distilled, passed over almost completely at 85—89°/12 mm., and had $n_D^{17°}$ 1·4541. The preparation of the derivatives described below showed it to consist essentially of *dl*-menthone, so that it was identical with product (5) and differed from products (3) and (6). *dl*-Menthone possesses a characteristic peppermint odour, which is if anything even more pronounced than that of *l*-menthone. *dl-iso*Menthone, on the other hand, has a decidedly fainter odour of the same general character.

Derivatives of dl-iso*Menthone*.—dl-iso*Menthoneoxime* was prepared from *dl-iso*menthone (b. p. 82—85°/8 mm.) obtained in preparation (3) above, by treatment in the usual way with hydroxylamine acetate (J., 1922, **121**, 586): 92·4 g. of the ketone yielded 100·4 g. of crude oxime, which crystallised partly when kept for a short time in a vacuum desiccator. The crystalline material (35 g.), dried on porous plate, melted indefinitely between 85° and 90°, but attained a constant m. p., 99—100°, after three recrystallisations from warm light petroleum. The substance is readily soluble in organic solvents, but when pure it crystallises from light petroleum with great ease in magnificent, transparent prisms, distinguished by their high lustre. The crystals were

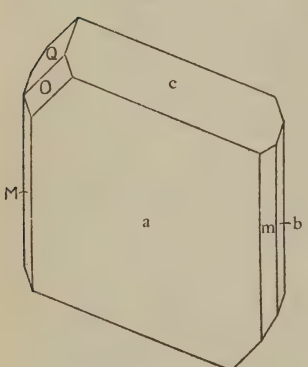
kindly measured by Mr. T. V. Barker, M.A., of the Department of Mineralogy, University of Oxford, who reports that they are anorthic with forms *a*, *m*, *b*, *M*, *c*, *Q*, and rarely *O*, developed in the proportions indicated by Fig. 1. The elements $a : b : c = 2{\cdot}049 : 1 : 1{\cdot}281$; $\alpha = 112°\ 12'$, $\beta = 116°\ 17'$, $\gamma = 86°\ 57'$, were computed from the following results of measurement of four crystals :

	a(100).	*m*(110).	*b*(010).	*M*($\bar{1}$10).	*c*(001).	*Q*(0$\bar{1}$1).	*O*(1$\bar{1}$1).
ϕ ...	0° 0′	0° 0′	0° 0′	0° 0′	*67° 48′	*134° 18′	134° 18′
ρ ...	0 0	56 51(14)	*82 6	*110 17	*62 48	75 23(3)	52 18(20)

Optically the extinction is nearly straight with the vertical edge, and an optic axis lies just within the field (Found : C, 71·1; H, 11·1. $C_{10}H_{19}ON$ requires C, 71·0; H, 11·2%).

The mother-liquors from the recrystallisation of the oxime deposited an oily product when concentrated by evaporation; when kept for some time, this material furnished a further quantity of the crystalline oxime described above, but no other crystalline oxime could be isolated. The lower fraction of *dl-iso*menthone (b. p. to 82°/8 mm,) from preparation (3) behaved similarly when oximated.

Fig. 1.



dl-iso*Menthoneoxime*.

*dl-iso*Menthone prepared by the catalytic reduction of *dl*-piperitone (6) gave a similar product, which, however, furnished a considerably higher proportion of the crystalline oxime. Fractions melting indefinitely between 60° and 75° were obtained from the mother-liquors, but no indication was forthcoming of the presence in these of *dl*-menthoneoxime.

Benzoyl-dl-iso*menthoneoxime* was prepared, by benzoylation in pyridine solution, as a viscid oil which was induced to crystallise with great difficulty. The crude product, after drying on porous plate, melted at 52—54°. After three successive recrystallisations from light petroleum, in which the derivative is very soluble, the melting point became constant at 55·5°, the pure substance separating in massive, transparent prisms suitable for goniometric examination. The product obtained by benzoylating the oily mother-liquor from the crystalline oxime could not be induced to crystallise (Found : C, 74·7; H, 8·9. $C_{17}H_{23}O_2N$ requires C, 74·7; H, 8·8%).

dl-iso*Menthone*iso*oxime*, prepared by dissolving crystalline *dl-iso*-menthoneoxime in cold concentrated sulphuric acid (Wallach, *Annalen*, 1894, **278**, 304), crystallised from hot water containing

a little alcohol in fine, glistening needles, m. p. 94—95°. The product of the reaction appeared to be homogeneous (Found: C, 70·2; H, 11·1. $C_{10}H_{19}ON$ requires C, 71·0; H, 11·2%).

Derivatives of dl-*Menthone.*—*dl*-Menthone from preparations (5) and (8) above, when oximated in the manner described for piperitone (J., 1922, **121**, 586), yielded *dl*-menthoneoxime (m. p. 81—82°) associated with a considerable amount of oily material. Unlike the stereoisomeric *dl-iso*menthoneoxime, this derivative could not be obtained in crystals sufficiently well developed for goniometric examination.

Attempts to benzoylate the crystalline oxime by the Schotten-Baumann method gave unsatisfactory results, but by the use of pyridine an oily product was obtained, which after extraction with ether and keeping in a vacuum desiccator crystallised spontaneously. The substance crystallised from light petroleum in small, transparent plates or glistening prisms, m. p. 72—73°. *Benzoyl*-dl-*menthoneoxime* is very soluble in all the usual organic solvents; it does not form such well-developed crystals as benzoyl-*dl-iso*-menthoneoxime (Found: C, 74·7; H, 8·6. $C_{17}H_{23}O_2N$ requires C, 74·7; H, 8·8%). The oily material from the mother-liquor of the crystalline *dl*-menthoneoxime yielded a viscid liquid when benzoylated in pyridine solution.

dl-*Menthone*isoo*xime*, prepared from crystallised *dl*-menthoneoxime in the manner indicated above, crystallised from hot water containing a little alcohol in fine, soft needles, m. p. 114—115°, and was readily obtained pure (Found: C, 69·9; H, 10·9. $C_{10}H_{19}ON$ requires C, 71·0; H, 11·2%).

Upon allowing *dl*-menthone (10·5 g.) to react with semicarbazide in the manner described in a previous paper (J., 1923, **123**, 2920), a crystalline product (10·2 g.) was readily isolated. By continued fractional crystallisation from hot methyl alcohol a small fraction of dl-*menthone-α-semicarbazone* was eventually obtained: this forms characteristic and well-defined, glistening prisms, m. p. 185—186° (Found: C, 62·1; H, 10·2. $C_{11}H_{21}ON_3$ requires C, 62·5; H, 10·0%). The bulk of the product, however, consisted of small, glistening needles of dl-*menthone-β-semicarbazone*, m. p. 161—162°; this derivative is more soluble than the isomeric compound (Found: C, 62·7; H, 10·3%). No semicarbazone characteristic of *dl-iso*-menthone could be isolated from this product; an intermediate product melting at about 177°, when mixed with *dl-iso*menthone-β-semicarbazone (m. p. 177—178°; J., 1923, **123**, 2922), softened at 158° and melted indefinitely between 169° and 176°. It may be remarked that *dl-iso*menthone-α-semicarbazone (m. p. 225°) is by far the least soluble of the semicarbazones of the optically inactive

menthones; its absence from the above reaction-product thus affords a criterion of the freedom of the specimen of *dl*-menthone from *dl-iso*menthone.

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University of St. Andrews. [*Received, July 6th*, 1925.]

CCCLXXXIV.—*The Ionic Activity Product of Water in Glycerol–Water Mixtures.*

By James Colvin.

Measurements have shown that a very marked increase occurs in the activity of hydrogen ion derived from hydrogen chloride in aqueous solution in the presence of a solvent-displacing agent, generally a non-electrolyte such as sucrose or glycerol (Moran and Lewis, J., 1922, **121**, 1613). It is of interest, therefore, to determine the activities of hydrogen and hydroxyl ions in a solution containing a substance such as glycerol, with a view to obtain the value of the ionic activity product of water, *i.e.*, the product of the hydrogen- and the hydroxyl-ion activities. Should the product remain constant, independent of the concentration of glycerol, it would permit of the determination of hydroxyl-ion activities by the hydrogen electrode, which is in many cases more convenient to use than a direct hydroxyl-ion electrode, such as the Donnan–Allmand electrode.

Measurements of the activities of hydrogen and hydroxyl ions were therefore carried out in solutions of $N/100$-sodium hydroxide, containing various amounts of glycerol.

Experimental.

The sodium hydroxide solution was prepared from metallic sodium and water free from carbon dioxide. The glycerol had been previously employed for conductivity measurements. For the measurements of the *E.M.F.* of the cells, a Cambridge–Paul potentiometer, reading to 0·1 millivolt, was used in conjunction with a mirror galvanometer. To avoid stray currents, the potentiometer and galvanometer were mounted on glass, insulated from earthed iron sheets by paraffin wax. The cells were maintained in a thermostat at a temperature of $25° \pm 0·05°$.

The Activity of Hydrogen Ion in Aqueous Solutions of Sodium Hydroxide and Glycerol.—The cell employed was of the following type :

$$- \begin{matrix}\mathrm{Pt}\\ \mathrm{H_2}\end{matrix} \Big| \begin{matrix}N/100\text{-NaOH}\\ \text{Glycerol}\end{matrix} \Big| \text{Sat. KCl} \Big| N\text{-Calomel} \Big| +$$

The electrode consisted of platinum foil, coated with platinum black, and was placed for 10 minutes in boiling water before use, following the procedure of Allmand (J., 1909, **95**, 2151). The hydrogen gas was prepared by the electrolysis of a solution of caustic soda and was washed by passing through a wash-bottle containing the solution under investigation. The gas thus being saturated with water vapour at the same pressure as the vapour pressure of the solution in the cell, no concentration changes could occur in the solution due to evaporation.

As some doubts have been expressed as to the trustworthiness and reproducibility of the hydrogen electrode in alkaline solution, it was thought advisable to carry out some preliminary measurements on the cell,

$$- \begin{matrix}\mathrm{H_2}\\ \mathrm{Pt}\end{matrix} \Big| N/10\text{-NaOH} \Big| \text{Sat. KCl} \Big| N\text{-Calomel} \Big| +$$

The following results were obtained :

Cell	1	2	3	4	5	6
E.M.F. (volts)	1·0412	1·0415	1·0411	1·0412	1·0415	1·0411

The mean value of the *E.M.F.*, 1·0413 volts, is in satisfactory agreement with the value, 1·0416 volts, obtained by Harned (*J. Amer. Chem. Soc.*, 1916, **37**, 2460).

As the reproducibility of the hydrogen electrode was thus satisfactorily demonstrated, measurements were made, using $N/100$-sodium hydroxide in presence of various amounts of glycerol. As the quantity of glycerol in the solution increased, a longer time was required for the electrode to attain equilibrium; in all cases, however, the values could be reproduced. The activities of the hydrogen ion were calculated by means of the formula $\pi_{H\cdot} = 0{\cdot}282 + 0{\cdot}059 \log_{10} a_{H\cdot}$. The absolute potential of the calomel electrode was taken to be 0·56 volt at 18°. The temperature coefficient of the electrode is 0·00068 volt per degree, hence the value at 25° is 0·5648 volt (compare Chroustchov and Sitnikov, *Compt. rend.*, 1889, **108**, 941).

The results obtained are in Table I.

The glycerol produces a very marked increase in the activity of hydrogen ion in the solution of alkali.

Table I.

G. of glycerol per 100 c.c.	*E.M.F.* in volt.	$-\pi_{H'}$.	$a_{H'} \times 10^{12}$.
0·0	0·9870	0·4222	1·16
12·6	0·9661	0·4013	2·62
20·0	0·9580	0·3932	3·60
25·2	0·9530	0·3882	4·40
40·0	0·9406	0·3758	7·06

The Activity of Hydroxyl Ion in Aqueous Solutions of Sodium Hydroxide and Glycerol.—The electrode employed was that described by Donnan and Allmand (J., 1911, **99**, 845) and consists essentially of a layer of mercuric oxide superimposed on a layer of mercury, the electrode vessel then being filled with the solution under investigation. The electrode reaction is given by the equation

$$HgO + H_2O + 2E = Hg + 2OH',$$

so that the equation for the electrode potential becomes

$$\pi_{OH'} = E'_0 - \frac{RT}{2F} \log \frac{a_{Hg} \times a^2_{OH'}}{a_{HgO} \times a_{H_2O}},$$

where E'_0 is the electrode potential in solutions where all the activities are equal to unity. Since the activities of the mercury and solid mercuric oxide are constant, they may be included in the first term on the right-hand side. For dilute solutions, the activity of the water remains sensibly constant. Hence the equation for the electrode potential in dilute solutions may be written

$$\pi_{OH'} = E_0 - 0{\cdot}059 \log_{10} a_{OH'}.$$

The value of the term E_0 was determined experimentally by the following method. The *E.M.F.* of the cell

$$- \text{Hg, HgO} \;\big|\; N/10\text{-KOH} \;\big|\; \text{Sat. KCl} \;\big|\; N\text{-Calomel} \;\big|\; +$$

was found to be 0·1178 volt at 25°. This gives the value 0·4470 volt as the electrode potential in $N/10$-potassium hydroxide. The activity of hydroxyl ion in the solution can be obtained from the data of Knobel (*J. Amer. Chem. Soc.*, 1923, **45**, 70) for the mean activity of potassium hydroxide in aqueous solution. On the assumption that the potassium ion has the same activity in solutions of potassium hydroxide and of potassium chloride of the same concentration, by employing the data of Noyes and MacInnes (*J. Amer. Chem. Soc.*, 1920, **42**, 239) for the activity of potassium ion in potassium chloride solutions, the value 0·0825 is obtained for the activity of hydroxyl ion in $N/10$-potassium hydroxide. By putting this value in the expression for the electrode potential, the value 0·3823 volt is obtained for E_0.

When glycerol is present, however, it is no longer justifiable to equate the activity of the water to unity. The expression for the electrode potential becomes

$$\pi_{OH'} = E_0 + (0{\cdot}059/2) \log_{10} a_{H_2O} - 0{\cdot}059 \log_{10} a_{OH'},$$

in which E_0 has the value found above.

Measurements with the Donnan–Allmand Electrode.—The mercury used in the cells was distilled in a vacuum. The mercuric oxide was prepared by heating the nitrate until no more brown fumes were evolved. The nitrate itself was prepared by acting on redistilled mercury with nitric acid (d 1·2) and recrystallising from nitric acid. The product thus obtained gave very reproducible results.

At first a large electrode vessel was used, but was soon discarded in favour of a smaller type, as equilibrium was then more readily attained. The cells set up were of the type

$$- \text{Hg, HgO} \;\Big|\; \begin{matrix} N/100\text{-NaOH} \\ \text{Glycerol} \end{matrix} \;\Big|\; \text{Sat. KCl} \;\Big|\; N\text{-Calomel} \;\Big|\; +$$

In all cases, readings of the *E.M.F.* were taken at intervals of 24 hours from the time of setting up the cell. In general, with N/100-sodium hydroxide alone present, equilibrium was attained within 48 hours. With glycerol present, the *E.M.F.* declined with time, hence a series of readings taken at intervals of 24 hours for the first 3 days were averaged to give the *E.M.F.* of the cell. As five cells for each concentration of glycerol were set up and the readings averaged, considerable confidence is placed in the results, which are in Table II. The activity of the water in glycerol–water mixtures may be obtained from the vapour pressure data of Perman and Price (*Trans. Faraday Soc.*, 1912, **8**, 74) at 70°. The activity of the water, which may be taken as the ratio of the vapour pressure of the solution to the vapour pressure of the solvent, is regarded as independent of the temperature (Lewis and Randall, "Thermodynamics," p. 349).

TABLE II.

G. of glycerol per 100 c.c.	*E.M.F.*	$\pi_{OH'}$.	a_{H_2O}.	$a_{OH'} \times 10^2$.
0	0·0604	0·5044	1·00	0·883
12·6	0·0394	0·5254	0·98	0·373
20·0	0·0314	0·5334	0·96	0·270
25·2	0·0266	0·5382	0·94	0·221
40·0	0·0147	0·5501	0·89	0·135

The glycerol produces a marked decrease in the activity of the hydroxyl ion.

The Ionic Activity Product of Water.—Sufficient data have now been obtained to calculate the ionic activity product and also the dissociation constant of water in presence of glycerol. The results are in Table III.

TABLE III.

G. of glycerol per 100 c.c.	$a_{H^{\cdot}} \times 10^{12}$.	$a_{OH'} \times 10^{2}$.	a_{H_2O}.	$a_{H^{\cdot}} \times a_{OH'} \times 10^{14}$.	$\frac{a_{H^{\cdot}} \times a_{OH'} \times 10^{14}}{a_{H_2O}}$
0	1·16	0·883	1·00	1·02	1·02
12·6	2·62	0·373	0·98	0·98	1·00
20·0	3·60	0·270	0·96	0·97	1·01
25·2	4·40	0·221	0·94	0·97	1·03
40·0	7·06	0·135	0·89	0·95	1·07

The value of the dissociation constant of water, *i.e.*, $a_{H^{\cdot}} \times a_{OH'}/a_{H_2O}$, remains practically constant over the whole range up to 40% of glycerol, the deviations from constancy being very small in comparison with the changes in the activities of the individual ions. At the same time, since the changes in the activity of the water effected by the presence of the glycerol are relatively small, the ionic activity product of the water maintains a reasonably constant value.

Summary.

1. Electrometric measurements of the activities of hydrogen ion in aqueous solutions of sodium hydroxide in presence of glycerol have been made at 25°.

2. The Donnan–Allmand electrode has been used to determine the activity of hydroxyl ion in solutions of sodium hydroxide containing glycerol.

3. The dissociation constant of water remains constant for the solutions containing up to 40% of glycerol; the ionic activity product does not exhibit appreciable change over the same range.

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CCCLXXXV.—*A Comparison of Methods of Measuring the Polarity* of Surfaces.*

By Neil K. Adam, Robert S. Morrell, and Ronald G. W. Norrish.

"Polarity" has been recently measured by Norrish (J., 1923, **123**, 3006), the measure being the catalytic activity of the surface for the combination of ethylene and bromine. Another measure of polarity is the attraction of a surface for water, or the work, W, required to separate the surface from water in contact with it; W is related to the angle of contact, θ, of water with the solid surface by the relation

$$W = T(1 + \cos\theta),$$

T being the surface energy of water (Adam and Jessop, this vol., p. 1863). Yet another indication of polarity is the objectionable property which some oil varnishes possess of condensing water on the varnished surface in a moist atmosphere and 'blooming.' Varnished surfaces which bloom easily may be considered more polar than non-blooming surfaces. This paper is an attempt to elucidate the nature of the "polarity" by comparing the results of the different methods of measurement.

Glass, stearic acid, paraffin wax, two non-blooming varnishes, A and B, and one blooming varnish, C, were compared. The non-blooming varnish film was composed of a hard copal resin incorporated in linoxyn containing lead and manganese catalysts. The blooming varnish film contained a rosin ester in tung oil "oxyn," with a manganese catalyst. Both for angle of contact and for catalysis measurements, the varnish was coated on glass and allowed to dry in a current of air (5 litres per hour) at 40—55° until constant in weight. The volatile thinners of the varnishes were expelled and the drying oils oxidised as completely as possible.

In the tables, k is the initial velocity coefficient, k' gives the catalytic effect in terms of k expressed as percentage of the value for glass, θ and W (ergs per sq. cm.) are defined above, and W' is the attraction for water as percentage of the attraction of water

* The terms "polar" and "non-polar" have become general in the sense that "polar" is applied to substances (and to groups therein) which tend to dissolve in water, and "non-polar" to those which dissolve in hydrocarbon solvents. This broad distinction of groups into two classes is a most useful working hypothesis for many investigations, and a more definite understanding of its nature and causes is much needed. The term "polarity" is here used in this sense, leaving entirely open the question whether there exists any resemblance to physical objects of unsymmetrical field of force, such as bar-magnets.—N. K. A.

for itself. The angle of contact method will not detect attractions for water greater than that of water for itself, attractions equal to and greater than this giving zero angle. Glass has an attraction for water at least as great as that of one water surface for another.

Catalytic action measured on dry ethylene and bromine.

Surface.	k.	k'.	θ.	W.	W'.
Glass	0·051	100	0°	not less than 146	100
Varnish A	0·048	94	95	66·6	45·5
Varnish C	0·112	220	60	109·5	75
Paraffin wax	0·003	6	105	54	37
Stearic acid	0·086	168	100	60·5	41

Catalytic action measured on moist ethylene and chlorine.

Glass	$9{\cdot}7\times10^{-4}$	100	0	146	100
Varnish B	4·0 ,,	41	95	66·6	45·5
Varnish C	11 ,,	113	65	104	71
Paraffin wax	0·01 ,,	0·1	105	54	37

The angle of contact measurements were made as described by Adam and Jessop, and are accurate to about 5°. The velocity coefficients for the ethylene–bromine reaction were determined as described by Norrish, fairly good constancy being obtained for the first five minutes of reaction. Ethylene and chlorine in the moist condition were employed for the second series, as it has been found possible thus to obtain more reproducible results than with dry ethylene and bromine; but owing to the higher pressure used there was appreciable attack of the varnish surfaces by the chlorine, which impaired the constancy of the velocity 'constants.' Details of the ethylene–chlorine method will be published shortly. The values, calculated as bimolecular coefficients, are given for the first two minutes of reaction, and afford a comparison of catalytic activity adequate for the present purpose. The figures for reaction rates are, of course, not comparable between the two series.

The angle of contact measurements were taken on the varnishes within a minute or two of immersion in the water. If allowed to soak, these surfaces gave an angle lower by 10° or, in some cases, 20°, the effect of soaking being more marked the greater the angle of contact.

Evidently the attractions for water parallel the veiling properties of the varnishes. It appears that if the attraction is more than about 70% of that of water for itself, the varnish veils; if less than 45 to 50%, it does not veil. We attempted also to grade varnishes in respect of their veiling properties by angle of contact measurements, but owing to the effect of soaking in water, these could not be made sufficiently accurately to distinguish varnishes with a

slight tendency to veil from non-veiling varnishes. The varnishes which were found to be more polar by the angle of contact method were also more polar by the catalytic measure.

There is, however, considerable disagreement between the polarities of the surfaces of different kinds as measured by the catalytic method and by angle of contact. Glass has less catalytic power than either stearic acid or the veiling varnishes, but very much greater attraction for water; and stearic acid, which has only a very slightly greater attraction for water than paraffin wax, has enormously greater catalytic activity. It would, of course, be possible to ascribe the difference to the " polarity " which causes attraction for water being of a different kind from that which confers catalytic activity; but such an *ad hoc* assumption would be particularly unreasonable, as it is not improbable that water itself is concerned in the catalysis. Adam and Jessop concluded that the evidence of angle of contact measurements on long-chain compounds pointed to the polar groups in stearic acid being buried in the interior. Hence it appears that in the catalytic measurements the reacting gases penetrated the surfaces to a short distance. The nature of the oxidised varnish surfaces is unknown: we consider it possible that ethylenic linkings are present. In this way it would be possible for the stearic acid and varnish surfaces to present more catalytically active groups than a glass surface, which must be presumed practically impermeable to the gases. By penetrating the solid to a depth of only the length of a few molecules, it would be possible for the gases to reach more polar groups than are to be found on an equal area of glass. If this is the correct explanation, it involves the assumption that the depth of the ' surface ' is much greater for the catalysis than for the angle of contact measurements. Varnishes differ in their absorption of, and permeability to, water, and no doubt to gases also; but we have not data enough to attempt a prediction of catalytic activity for different varnished surfaces, taking this factor into account. This factor of permeability requires further investigation; in Adam and Jessop's paper some evidence was given that there is more depth involved in the case of crystal flakes of the long-chain amine hydrochlorides than with the other long-chain aliphatic substances used. Nevertheless we feel that, qualitatively, it supplies an adequate reason for the difference in behaviour of different ' surfaces ' to reagents.

Paraffin wax is not a catalyst, because no matter how far the gases may diffuse into the interior, no polar groups are encountered.

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CCCLXXXVI.—*An Electrometric and a Phase Rule Study of some Basic Salts of Copper.*

By Hubert Thomas Stanley Britton.

This paper deals with experiments made to ascertain which of the many basic sulphates and chlorides of copper are definite compounds. Basic sulphates have been reported ranging in composition from $2CuO,SO_3$ to $15CuO,SO_3$, with varying water contents. Pickering (J., 1910, **97**, 1851) regarded the latter as a complex salt of orthosulphuric acid and bivalent and what he supposed to be quadrivalent copper atoms, and Noyes (*J. Amer. Chem. Soc.*, 1916, **38**, 1947) suggested that $3CuO,SO_3,2H_2O$ might be the dihydrated cupric salt of the same acid. The basic chlorides which have been described contain from 1 to 4·5 atoms of copper for each atom of chlorine. Naturally occurring basic sulphates and chlorides are langite, $4CuO,SO_3,4H_2O$; brochantite, containing from 3 to 4 mols. of CuO for 1 mol. of SO_3, together with varying amounts of water, and atacamite, $4CuO,2HCl,3H_2O$—the number of molecules of water varying from 2 to 5.

Bell and Taber (*J. Physical Chem.*, 1908, **12**, 171) and Young and Stearn (*J. Amer. Chem. Soc.*, 1916, **38**, 1947), who studied the basic sulphates of copper from the point of view of the phase rule, obtained very conflicting results and were unable to prove the existence of a definite basic sulphate; doubtless because they used substances which approached equilibrium very slowly.

It has long been known that an amorphous, blue precipitate, agreeing very closely in composition with $4CuO,SO_3,4H_2O$, is produced by treating copper sulphate solution with an insufficiency of alkali (Kane, *Ann. Chim. Phys.*, 1839, **72**, 270; Smith, *Phil. Mag.*, 1845, **23**, 501; Field, *ibid.*, 1862, **24**, 124). Williamson (*J. Physical Chem.*, 1923, **27**, 790) analysed the precipitates obtained by treating molar solutions of copper sulphate with different quantities of alkali. Pickering showed (*Chem. News*, 1883, **47**, 181) that between 1·4 and 1·5 equivalents of potassium hydroxide completely precipitated the copper and that the amount precipitated at any stage of the reaction was directly proportional to the amount of alkali added. He also found a temporary alkalinity to phenolphthalein when 1·5 equivalents of alkali had been added. Similar observations were made by the author, using the oxygen electrode (this vol., p. 2152).

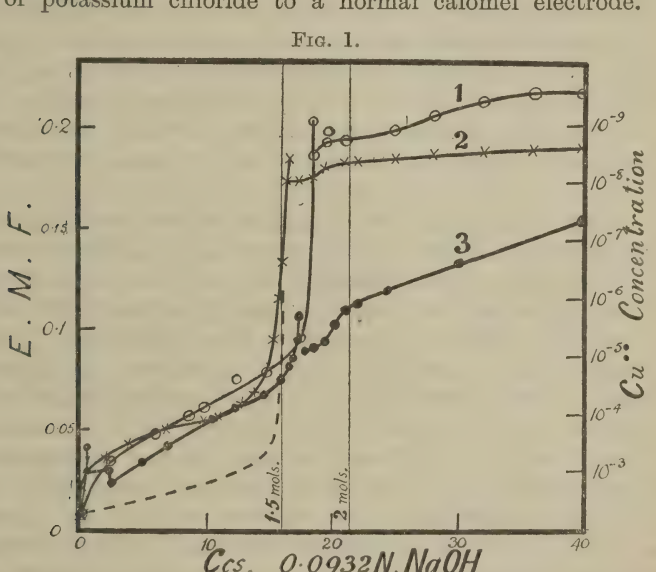
Apart from the little recorded by Kenrick and Lash Miller (*Trans. Roy. Soc., Canada*, 1901, **7**, iii, 35), no systematic work has been done on basic cupric chloride. The precipitate formed

when $N/5$-copper chloride solution was treated at 85° with $N/5$-potassium hydroxide until all the copper had been precipitated had the formula $CuCl_2,3CuO,2H_2O$.

Experimental.

In order to study the mode of precipitation of copper sulphate by sodium hydroxide, electrometric titrations with a copper electrode were carried out. A copper wire electrode, fused into a glass tube, was completely immersed in 100 c.c. of $M/100$-copper sulphate solution, which was connected through a saturated solution of potassium chloride to a normal calomel electrode. The

Fig. 1.



E.M.F.'s between the copper and the calomel electrodes were measured by means of a potentiometer and a capillary electrometer. The electrode was about 2 mm. in diameter and was covered with finely divided copper, deposited electrolytically from $N/10$-copper sulphate solution. That electrodes so prepared worked satisfactorily in copper sulphate solution will be seen from the following measurements. At 20°, the *E.M.F.* of the cell Cu | 0·01M-$CuSO_4$ | saturated KCl | N-calomel was − 0·006 volt. Therefore E_h Cu | 0·01M-$CuSO_4$ = + 0·283 − 0·006 = 0·277 volt. 0·01M-Copper sulphate being taken as 54·7% dissociated ($\Lambda_\infty = 114$, and $\Lambda_{0\cdot01M} = 62{\cdot}4$), $0{\cdot}277 = EP_{Cu_h} + 0{\cdot}029 \log 0{\cdot}00547$. Whence $EP_{Cu_h} = 0{\cdot}343$, which is in agreement with the recent value of Jellinek and Gordon (*Z. physikal. Chem.*, 1924, **112**, 214).

Three typical titration curves are given in Fig. 1. The cupric-

ion concentration scale was calculated from the formula $E_{obs.} = -0{\cdot}060 - 0{\cdot}029 \log [Cu^{\cdot\cdot}]$. The dotted line gives the theoretical change in copper-ion concentration calculated on the assumption that $4CuO,SO_3$ alone is precipitated. Curves 1 and 2, plotted from results obtained with an electrode having a thin coating of copper (deposited during 5 minutes' electrolysis), and curve 3 (electrode heavily coated during 1 hour's electrolysis) show that the electrodes became untrustworthy as soon as a precipitate appeared. Deduced from the curves, the values for the concentrations during precipitation are much too small and those for the concentrations when precipitation was complete and the solutions had become alkaline are obviously too large. High *E.M.F.*'s were obtained immediately precipitation was complete, but these fell in the course of 5 minutes to more or less steady values. The effect of the heavy deposit (curve 3) was to render the electrode even more irregular, as may be seen from the second portion of the curve.

The curves show that sudden changes in copper-ion concentration occurred when 1·73 (curve 1), 1·5 (curve 2), and 1·63 equivalents (curve 3) of sodium hydroxide had been added. In titration 2, the alkali was added very slowly, and the mixture was stirred until any green, gelatinous precipitate which might have formed had become pale blue and apparently amorphous. In the other two titrations the alkali was added more rapidly and, although the reactants were thoroughly mixed, stirring was not maintained until the precipitate appeared to have become homogeneous. These experiments show once again that the nature of the precipitate obtained depends on the manner in which the alkali is added. Rapid addition necessitated the use of a larger quantity for complete precipitation and consequently the gelatinous precipitate obtained was more basic than the blue, amorphous * precipitate produced on careful addition of the alkali. This is the reason why Harned (*J. Amer. Chem. Soc.*, 1917, **39**, 252) required in his similar titration of copper sulphate solution six-sevenths of the theoretical quantity of the alkali.

The Anomalous Behaviour of Copper Electrodes in Presence of Copper Hydroxide.—The foregoing observations become of importance in view of the recent measurements of Jellinek and Gordon (*loc. cit.*) of the solubility product of cupric hydroxide.

* Here and elsewhere in this paper, the term "amorphous precipitate" is used to denote the non-gelatinous, apparently amorphous precipitates obtained when alkali hydroxide is added slowly to dilute solutions of cupric salts. They are sharply distinguished from the gelatinous precipitates produced by rapid mixing.

They precipitated their copper hydroxide from copper sulphate solution with an insufficiency of sodium hydroxide—exactly the condition for obtaining basic copper sulphate! The washed precipitate was suspended in alkali solution, and the copper-ion concentration was measured by means of a copper electrode. Their values for $[Cu^{\cdot\cdot}][OH']^2$ at 20° varied from $0{\cdot}7 \times 10^{-13}$ to $3{\cdot}0 \times 10^{-13}$, the mean being $1{\cdot}7 \times 10^{-13}$, but they could not confirm this by measurements with copper oxide. It is interesting to compare these values with those obtained from the curves (Fig. 1), assuming for the moment that the observed *E.M.F.*'s gave a true measure of the copper-ion concentration and that the basic precipitates had been completely decomposed by the excess of alkali. The hydroxyl-ion concentration when 40 c.c. of 0·0932*N*-sodium hydroxide had been added, the ionisation of the alkali being assumed to be complete, was $10^{-1{\cdot}91}$, and the cupric-ion concentration was $10^{-9{\cdot}55}$ (curve 1; *E.M.F.* = 0·217 volt), $10^{-8{\cdot}62}$ (curve 2; *E.M.F.* = 0·190 volt), and $10^{-7{\cdot}59}$ (curve 3; *E.M.F.* = 0·160 volt). Therefore $[Cu^{\cdot\cdot}][OH']^2$ is 4×10^{-14} (curve 1), $3{\cdot}6 \times 10^{-13}$ (curve 2), and $3{\cdot}9 \times 10^{-12}$ (curve 3). Although these values are meaningless, they are of the same order as those of Jellinek and Gordon. The precipitation of basic copper sulphate does not begin until p_H 5·6 has been attained, and from the method described by the author (*loc. cit.*), the presence of the sulphate in the precipitate being assumed not to affect greatly the precipitation p_H, it follows that the solubility product of cupric hydroxide is probably of the order 10^{-20}.*

Jellinek and Gordon do not refer to the work of Immerwahr (*Z. anorg. Chem.*, 1900, **24**, 269) on the potentials of copper electrodes in baryta solutions containing colloidal copper hydroxide or ignited copper oxide. The *E.M.F.*'s were so irregular that she did not calculate the solubility product of cupric hydroxide. Calculation shows that the solubility product varies from 3×10^{-12} to 8×10^{-16} for the colloidal hydroxide and to 8×10^{-23} for the ignited oxide. Allmand (J., 1909, **95**, 2151) traced the erratic behaviour of the copper electrode to the reaction $Cu^{\cdot\cdot} + Cu \rightleftharpoons 2Cu^{\cdot}$ taking place at the electrode, cuprous hydroxide being formed, and arrived by an indirect method at the value 10^{-19} for the solubility product of cupric hydroxide, which is of the same order as that calculated from the precipitation p_H, *viz.*, 10^{-20}. Jellinek and Gordon, who stated that to their knowledge no value for the solubility

* For the titration given in this vol., p. 2151, the limiting $[Cu^{\cdot\cdot}]$ was equivalent to 0·6 c.c. of *N*/10-sodium hydroxide in 120 c.c. Therefore $[Cu^{\cdot\cdot}] = 0{\cdot}3/120M/10 = 10^{-5{\cdot}6}$. $[OH'] = 10^{-14+5{\cdot}6} = 10^{-8{\cdot}4}$. Whence $[Cu^{\cdot\cdot}][OH']^2 = 10^{-20}$.

product of cupric hydroxide is recorded in the literature, had evidently not seen Allmand's paper.

This reducing action of the copper electrode accounts for its irreversible behaviour in the titrations, and the exceptionally low voltages obtained in No. 3 show that the reduction process was being considerably influenced by the nature of the layer deposited on the electrode.

The System CuO–SO_3–H_2O *at* 25°.—The substances used in the investigation were selected for their capacity to enter rapidly into equilibrium, namely, the amorphous basic sulphate, free sulphuric acid, and copper sulphate solution. The stock basic sulphate was kept as reactive as possible by suspending it in water. For certain equilibria, wet hydrated copper oxide had to be used.

The amorphous basic sulphate was prepared by adding *N*/10-sodium hydroxide (about 1·2 mols. for each mol. of copper sulphate) drop by drop and with continuous shaking to 10 litres of *M*/20-copper sulphate, every care being taken to prevent the formation of any gelatinous precipitate. The precipitate was washed by decantation with 20 to 30 litres of water, pressed on a Büchner funnel, and immediately immersed in water (Found in air-dried samples: CuO, 67·2, 67·6; SO_3, 17·1, 17·2. $4CuO,SO_3,4H_2O$ requires CuO, 67·7; SO_3, 17·0%). On keeping the precipitate, which was quite insoluble in water, in different quantities of sulphuric acid over-night, in every case 1·33 mols. of copper sulphate passed into solution for each molecule of sulphuric acid employed, thereby showing that the ratio of copper to sulphate in the residual solid remained unaltered, *viz.*, 4 : 1.

Quantities of the basic sulphate were placed in liquid phases (100 to 200 c.c.) composed of sulphuric acid and copper sulphate in various proportions, the quantities of acid being such that the rests should be small (about 2 g.). The mixtures were placed in a thermostat at 25° and shaken daily. Equilibrium was attained in less than a week, but 2 or 3 months were allowed to elapse before the final check analyses were made. The results shown in the most basic part of the isotherm necessitated the use of hydrated copper oxide. This was prepared by precipitation from a dilute copper sulphate solution at about 50° with a small excess of sodium hydroxide. It was somewhat dehydrated and brownish-black, but it had to be deposited at a moderately high temperature so that it should not be so gelatinous that it could not be washed free from alkali and sodium sulphate. This hydrated oxide was also used with sulphuric acid to confirm some determinations of the equilibria of mixtures prepared from the basic sulphate. The analyses of the various liquid phases and rests are in Table I.

TABLE I.

Liquid phases.		Rests.			
% CuO.	% SO_3.	% CuO.	% SO_3.	Mol. SO_3/ mol. CuO.	Solid phases.
0	0	84·45	6·17	0·073	CuO (hydrated) and $4CuO,SO_3,4H_2O$.
0	0	80·85	8·79	0·108	" "
0	0	77·56	11·77	0·151	" "
0	0	73·75	13·82	0·186	" "
0	0	69·50	16·90	0·242	" "
0	0	67·78	17·30	0·255	" "
0·02	0·02	67·90	17·60		$4CuO,SO_3,4H_2O$.
0·09	0·09	26·36	6·77		"
0·12	0·12	9·24	2·43		"
0·58	0·58	7·89	2·46		"
3·17	3·19	31·23	9·85		"
5·54	5·56	15·96	7·75		"
7·17	7·18	24·10	10·27	0·314	"
9·28	9·33	Eutectic			$4CuO,SO_3,4H_2O$ and $CuSO_4,5H_2O$.

The first six sets of data show that the addition of sulphuric acid to the hydrated copper oxide failed to cause any solution until the solid phase had assimilated sufficient sulphuric acid to convert it into the basic sulphate containing 4CuO to $1SO_3$. Neither copper nor sulphate could be found in the colourless liquid phases. The analyses given are those of the air-dried solid phases. These changed in colour as their sulphate content increased, passing from the brownish-black of the hydrated oxide through increasingly brighter shades of brown to greenish-brown and finally to the greenish-blue colour of the 4 : 1 salt. The basic sulphate did not change in colour on boiling, but decomposed on addition of varying quantities of alkali, yielding more basic products having similar colours. The other liquid phases were copper sulphate.

The results given in Table I are plotted in Fig. 2; the section BC has been constructed from the data of Bell and Taber (*loc. cit.*). The solid phase which was in equilibrium with the liquid phases represented by AB was $4CuO,SO_3,4H_2O$, for the tie-lines joining the points corresponding to each liquid phase and the point corresponding to its respective rest all pass through the point D, which indicates that the solid phase contained 67·7% CuO, 17·0% SO_3, and 15·3% H_2O (Schreinemakers). Had the solid phases in equilibrium with water as liquid phase been mixtures of two definite solid phases, it would have been expected that the points representing their compositions would lie on the straight line joining the two points corresponding to the compositions of the two solid phases. If in the present system the rests comprised mixtures of the basic salt $4CuO,SO_3,4H_2O$ and a definitely hydrated copper oxide, this line would have been one joining the point D to the

point, corresponding to the particular hydrated oxide, on the H_2O–CuO axis. Actually the points lie on one of two straight lines, DE and DF, where E represents $CuO,0{\cdot}28H_2O$ and F, $CuO,0{\cdot}05H_2O$. It appears from the phase rule that as the liquid phases which were in equilibrium with these highly basic rests were of fixed composition as far as could be ascertained, the rests were composed of two solid phases. Bearing in mind the gradual change in the colour of the rests, it seems probable that the two solid phases were the 4 : 1 sulphate and copper oxide, hydrated to varying extents. The degree of hydration of the copper oxide, although by no means fixed, was of the same order as that found in the ordinary precipitated black copper oxide, *i.e.*, corresponding approximately to $CuO,0{\cdot}25H_2O$. There appeared, however, a tendency for the hydration to become considerably less as the proportion of the 4 : 1 salt became predominant, shown by those points which fall on DF.

It follows from this work that at 25° there is only one basic sulphate of copper, *viz.*, $4CuO,SO_3,4H_2O$. Sabatier (*Compt. rend.*, 1897, **125**, 101) prepared it from copper oxide and copper sulphate solutions (not exceeding 1*M*). He stated that the salt was converted by saturated copper sulphate solution into a green salt, $5CuO,2SO_3,5H_2O$, treatment of which with water regenerated the 4 : 1 salt. This green salt was probably the ordinary 4 : 1 salt with copper sulphate adhering. In support of this view is the fact that the rest belonging to the liquid phase which contained 7·17% CuO (Table I) had, after filtration on a Büchner funnel, a composition corresponding approximately to the formula $3CuO,SO_3$, although, as its tie-line shows, the actual solid phase was the 4 : 1 salt.

Precipitation of Basic Cupric Chloride.—When *N*/10-sodium hydroxide or ammonia was added slowly with shaking to *M*/100-cupric chloride solutions, pale blue, amorphous precipitates were obtained, and the mother-liquors became alkaline to phenolphthalein, precipitation being complete, after the addition of 1·5 equivalents of alkali. If the additions were made quickly, precipitates did not separate until about 1 equivalent of alkali had been added, but the solutions became more and more colloidal and alkalinity occurred after the addition of 1·53 equivalents. When, however, more concentrated solutions were rapidly mixed, dark blue, gelatinous precipitates were obtained which, if the amount of alkali added did not exceed 1·5 equivalents, could be transformed by vigorous shaking with the mother-liquor into paler blue, amorphous forms. Provided that not more than 1·5 equivalents of alkali had been added during their formation, the amorphous precipitates did not

blacken on boiling; if a precipitate happened to be gelatinous, it darkened temporarily, but became pale blue and amorphous on continued boiling.

The System CuO–HCl–H_2O *at* 25°.—This system was investigated in exactly the same manner as the previous one. The substances used were moist hydrated copper oxide, moist basic cupric chloride, hydrochloric acid, and cupric chloride solution. On being washed by decantation, much of the basic chloride passed into pale blue, colloidal solution, and did not settle out after standing for a week. The colloidal solution was siphoned off and replaced by water, and the process was repeated, during a month, until the remaining precipitate was free from impurities. Samples which had been either air-dried or dried over fused calcium chloride agreed closely in composition with the formula $4CuO,2HCl,3H_2O$ (Found: CuO, 72·0; HCl, 16·5. Calc., CuO, 71·5; HCl, 16·4%). The salt was amorphous and insoluble in water; but after it had been boiled with water, the latter gave a faint opalescence with silver nitrate.

Equilibrium was attained in about a week, but the final analyses were not made until 3 months had elapsed.

The first four sets of data in Table II refer to solid phases which had been air-dried. The liquid phases were water. No copper chloride dissolved until each molecule of hydrated copper oxide had reacted with 0·5 equivalent of hydrochloric acid. Thereafter the solid phase was $4CuO,2HCl,3H_2O$, as shown by the point of intersection of the tie-lines in Fig. 3, and the liquid phases contained cupric chloride only.

TABLE II.

Liquid phases.		Rests.			
% CuO.	% HCl.	% CuO.	% HCl.	Mol. HCl/ mol. CuO.	Solid phases.
0	0	90·28	0·03	0·001	CuO (hydrated) and $4CuO,2HCl,3H_2O$.
0	0	79·30	11·49	0·315	,, ,,
0	0	74·07	14·90	0·438	,, ,,
0	0	72·47	16·57	0·499	$4CuO,2HCl,3H_2O$.
0·16	0·15	52·80	12·56	0·517	,,
3·90	3·57	55·37	13·49		,,
8·35	7·66	56·45	14·60		,,
15·22	13·96	56·04	16·35		,,
18·52	17·03	55·72	16·90		,,
21·24	19·49	51·67	18·14		,,
25·59	23·51				$4CuO,2HCl,3H_2O$ and $CuCl_2,2H_2O$.

The rests which had attained equilibrium with water, after being allowed to settle for a month, presented a striated appearance, pale green layers underlying layers of varying shades of dark

brown. The layers were roughly separated from one another by spraying with a very fine jet of water. The uppermost contained the least chloride, about 0·1 equivalent for each molecule of copper oxide, and the bottom pale green layers contained the most, about 0·3 equivalent. It was not possible to isolate the bottom layers quite free from the more basic, brown particles; probably the amount of chloride actually present in them was greater than 0·3 equivalent.

These observations seem to indicate that each of the highly basic rests was composed of a mixture of two solid phases as required

FIG. 2.

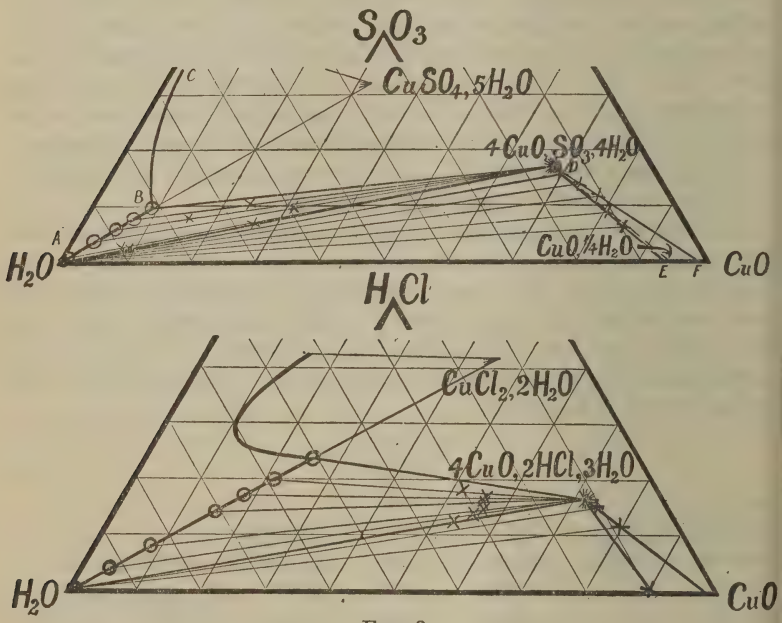


FIG. 3.

by the phase rule, and from Fig. 3 there appears to be no doubt that these were the definite basic chloride (greenish-blue) and dark brown copper oxide of varying hydration.

The basic chloride $4CuO,2HCl,3H_2O$ and the rests which contained more than 0·315 equivalent of chloride tended to pass into colloidal solution. Attempts were made to get some idea of the composition of the colloidal suspensions, and it was found that the basic chloride aggregates contained from 0·27 to 0·33 equivalent of chloride for each molecule of copper oxide.

The curve in Fig. 3 corresponding to those liquid phases which

exist in equilibrium with dihydrated cupric chloride was drawn from Foote's data (*J. Amer. Chem. Soc.*, 1923, **45**, 663).

Basic Cupric Nitrate.—Several basic nitrates have been described containing from 1·7 to 3 atoms of copper for each molecule of nitrate. The pale bluish-green precipitate formed when alkali, insufficient for complete reaction, is added to a dilute cupric nitrate solution has been shown by many workers to correspond to the formula $4CuO,2HNO_3,2H_2O$. The mineral gerhardtite has the same composition; in some specimens, however, the water content appears to be $1H_2O$.

When *N*/10-sodium hydroxide was carefully added to cupric nitrate solution, precipitation was complete and the solution became alkaline to phenolphthalein after the addition of 1·5 equivalents. The composition of the precipitate agreed with the above formula (Found: CuO, 66·8; HNO_3, 26·4. Calc., CuO, 66·3; HNO_3, 26·2%). The basic nitrate was insoluble in water, but on boiling with water it soon blackened and some passed into colloidal suspension. The salt was also much more readily decomposed by alkali than was either the sulphate or the chloride, so much so that when alkali was added rapidly to a cupric nitrate solution alkalinity was not produced until 1·9 equivalents had been added.

Basic Cupric Bromide.—The basic bromide produced by the oxidation of cuprous bromide and by the prolonged digestion of a solution of cupric bromide with copper oxide (Richards, *Chem. News*, 1891, **63**, 75; Sabatier, *Compt. rend.*, 1897, **125**, 103) has the formula $4CuO,2HBr,2H_2O$. The substance produced on gradual addition of alkali to cupric bromide solution has apparently not been examined. *N*/10-Sodium hydroxide gave a pale blue, amorphous precipitate and the mother-liquor became alkaline to phenolphthalein after approximately 1·5 equivalents had been added. This result suggests that the precipitate contained CuO and HBr in the molar ratio of 2 : 1. The (air-dried) precipitates formed by varying amounts of alkali, however, were slightly more basic [Found: (*a*) CuO, 60·55; HBr, 29·4. (*b*) CuO, 61·0; HBr, 30·3, corresponding respectively to $4CuO,1·91HBr,2·93H_2O$ and $4CuO,1·95HBr,2·52H_2O$]. It is fairly certain that they were essentially the 4 : 2 bromide, although the data are insufficient to state what was the exact water content. The basic bromide was insoluble in water and did not blacken when boiled with it. In common with the basic nitrate and the basic chloride, it had a marked tendency to pass into colloidal suspension when treated with water.

Discussion.

It has been shown that of the many basic sulphates and chlorides of copper which have been reported, only one definite sulphate and one definite chloride exist at 25°, *viz.*, $4CuO,H_2SO_4,3H_2O$ and $4CuO,2HCl,3H_2O$. Similar nitrate and bromide compounds have been shown to be produced by precipitation with alkali under similar conditions, *viz.*, $4CuO,2HNO_3,2H_2O$ and $4CuO,2HBr,2(?)H_2O$. They are similar not only in composition, but also in form, colour, and insolubility. All these salts are precipitated from solution at hydrion concentrations of about $10^{-5\cdot6}$. The similarity in their composition seems to be due to an intrinsic property of either the copper atom or the copper oxide molecule.

Previous workers have attempted to account for the sulphate and the nitrate as complex salts of ortho-acids, but such an explanation cannot be applied to the basic chloride or the basic bromide. The usual way of representing these basic salts as if they were double salts, *e.g.*, $CuSO_4,3Cu(OH)_2,H_2O$, is unsatisfactory, for they have none of the properties of double salts inasmuch as they are insoluble. Werner (*Ber.*, 1907, **40**, 4444), on the basis of his co-ordination theory, regards them as the normal salts of a hypothetical hexolcupric base, *e.g.*, $\left[Cu\left(\begin{matrix}HO\\HO\end{matrix}\!\!>\!Cu\right)_3\right]SO_4,H_2O$. This representation seems to be equally open to objection. Such a constitution would suggest that, contrary to the facts, the salt has to some extent the capacity of dissolving, which by comparison with difficultly soluble salts of metals, *e.g.*, lead and silver, is in some way connected with the nature of the acid radical, and would ionise in solution into "hexolcupric" and sulphate ions. The comparative inertness of these basic compounds to reaction and their similarity in properties to copper hydroxide seem to show that they are essentially compounds of this base of some unknown kind. Until something is known about their constitution it is perhaps better to represent them thus, $Cu_4(OH)_6SO_4,H_2O$. Were it known that the co-ordination number of bivalent copper is 6, the Werner theory might be considered to supply a tentative explanation why these basic salts contain copper and the acid in the equivalent ratio of 4 : 1. The ammine compounds of cupric salts have such widely varying compositions that no definite co-ordination number can be assigned. If the constitution of the cupric complexes in ammoniacal solutions be considered, the co-ordination number is probably 4.

Chatterji and Dhar state (Discussion on Colloids, *Faraday and Phys. Soc.*, 1920, 124) that the blackening on boiling of copper hydr-

oxide can be prevented by the addition of a little normal salt, which is adsorbed and thus renders the copper hydroxide stable. They do not appear to have considered what may be the effect of the formation of basic salts. The retention of the colour on boiling is a property of such salts—less marked, it is true, in the case of the nitrate (see pp. 2801, 2803, 2805).

Since the foregoing pages were written, Krüger has published some work on the basic sulphates of copper (*J. pr. Chem.*, 1924, **108**, 278). He obtained a product having the formula $4CuO,SO_3,4H_2O$, and also basic sulphates whose analyses, although irregular, indicated the formulæ $4CuO,SO_3,3{\cdot}5H_2O$, $4CuO,SO_3,5H_2O$, and $3CuO,SO_3,2{\cdot}5H_2O$. The water contents of the first two of these three substances are probably due to imperfect purification, and the last is undoubtedly a mixture of the definite basic salt and copper sulphate.

Summary.

(1) According to the manner of mixing and the quantity of alkali used, either apparently amorphous or gelatinous precipitates may be obtained by adding alkalis to solutions of the sulphate, chloride, bromide, or nitrate of copper.

(2) The individualities of the basic salts $Cu_4(OH)_6SO_4,H_2O$ and $Cu_4(OH)_6Cl_2,H_2O$ have been established.

(3) The behaviour of the $Cu|Cu(OH)_2,NaOH$ electrode has been shown to be erratic, and the value of Jellinek and Gordon for $[Cu^{\cdot\cdot}][OH']^2$ untrustworthy.

(4) Observations have been made on the darkening of suspensions of basic copper salts on boiling.

(5) The constitutions of the basic salts have been discussed with special reference to Werner's co-ordination theory.

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CCCLXXXVII.—*The Relationship between the Optical Rotatory Powers and the Relative Configurations of Optically Active Compounds. Part II. The Relative Configurations of the Optically Active Mandelic Acids and β-Phenyl-lactic Acids.*

By GEORGE WILLIAM CLOUGH.

IN Part I * (J., 1918, **113**, 526) it was shown that the formation of similar derivatives from the configuratively related compounds, *l*-lactic acid, *l*-glyceric acid, *d*-malic acid, and *d*-tartaric acid, was usually accompanied by changes of the same character in their optical rotatory powers. It was therefore assumed that, as a rule, the introduction of the same substituent into similarly constituted, optically active compounds possessing the same relative configurations produced alterations of the same character in their optical rotatory powers. The somewhat vague term "similarly constituted compounds" was used in this connexion, since it was not (and still is not) possible to state precisely the extent of the applicability of the rule. It applies to the members of such homologous series of optically active compounds as the aliphatic normal secondary alcohols and the simple α-hydroxy-acids. Indeed, the higher members of a homologous series being derivatives from the lower members, the rule would indicate that the optical rotatory powers of those optically active members of a series which are configuratively related would lie approximately on a curve. But not only do regularities occur in the optical rotatory powers of members of homologous series, they are evident (with few exceptions) in those of corresponding derivatives from the optically active mono- and di-hydroxy-propionic and -succinic acids.

The application of the principle to *d*-α-hydroxybutyric acid left no doubt that this compound possessed the same configuration as *l*-lactic acid, but the same confidence could not be felt in the conclusions which were drawn from the optical rotatory powers of compounds in which a phenyl or benzyl group was attached to the asymmetric carbon atom. In an endeavour to fix definitely the

* Errata in Part I: Page 532, line 5 from bottom, *for* "X=Bz, Y=Me" *read* "X=Bz, Y=Et."

Page 532, last line, *for* "−123·6" *read* "−247."

Page 540, line 3, *for* "+50·6°" *read* "−50·6°."

Since this paper was submitted for publication, the author's attention has been directed to a paper by Freudenberg and Markert entitled "Die Konfiguration der Mandelsaure" (*Ber.*, 1925, **58**, 1753). These authors have employed the method indicated in Part I and have confirmed the suggestion made therein concerning the configurations of the optically active mandelic acids.

configurations of the optically active forms of mandelic and β-phenyl-lactic acids, the optical rotatory powers of these compounds and some of their derivatives are considered in the present communication. The measurement by Freudenberg, Brauns, and Siegel (*Ber.*, 1923, **56**, 199) of the specific rotation of the amide of *l*-hexahydromandelic acid (prepared from *l*-mandelic acid) enabled those workers to confirm the suggestion that *l*-mandelic acid is a "*d*"-α-hydroxy-acid (Part I, p. 534). (For compounds containing one asymmetric carbon atom it appears to the present author desirable to retain the prefixes *d*- and *l*- with their conventional significance, but to denote their relative configurations by the prefixes "*d*"- and "*l*"-; *loc. cit.*, p. 534.) The optical rotatory powers of other derivatives from *l*-hexahydromandelic acid and from *l*-mandelic acid definitely indicate that these acids belong to the "*d*"- series of α-hydroxy-acids. This result is of importance in that it enables us to determine the configurations of *l*-benzoin, the related optically active glycols and of amygdalin with reference to that of *d*-tartaric acid. The experimental data quoted in tables I—V are also, in the author's opinion, sufficient to justify the allocation of *d*-β-phenyl-lactic acid to the "*d*"- series of α-hydroxy-acids. If this conclusion is accepted, it is possible to assign configurations to the glycols derived from this acid and also to the four optically active phenylglyceric acids (provided the assumption is made that *cis*-addition of hydroxyl occurs on oxidation of the cinnamic acids; compare Berner and Riiber, *Ber.*, 1921, **54**, 1945).

The molecular rotations of the standard "*d*"- acids in aqueous solution are lower * than those of the corresponding sodium (potassium or ammonium) salts (Table I). The same regularity is observed in the molecular rotations of *l*-hexahydromandelic acid, *l*-mandelic acid, *d*-β-phenyl-lactic acid and their salts.

The molecular rotations of the lower esters of the same acids increase as the molecular weights of the esters increase (Table II). The measurements by Wood and his collaborators of the optical rotatory powers and the optical dispersive powers of the optically active alkyl lactates and hexahydromandelates at various temperatures are especially valuable in connexion with the subject of this investigation.

The molecular rotations of the amides of the same acids compared with those of the methyl esters further illustrate the relation of

* Throughout this paper an "increase" of rotation denotes an increase in the numerical value of a dextrorotation or a decrease in the numerical value of a lævorotation. For the sake of clearness, the tabulated values are given for the "*d*"-forms, although in some cases the measurements were actually made on the enantiomorphous forms.

l-mandelic acid and of *d*-β-phenyl-lactic acid to the standard "*d*"-α-hydroxy-acids (Table III).

TABLE I.

The Molecular Rotations ($[M]_D$) *of Some Optically Active α-Hydroxy-acids in Aqueous Solution.*

Acid.	Sodium salt.	Potassium salt.	References.
l-Lactic acid.	−2° (*c* = 5)	+ 13·2°	+13·7° Purdie and Walker, J., 1895, **67**, 630.
l-Glyceric acid.	−2·3 (*c* = 20)	+ 20·6	+23·7 Frankland and Appleyard, J., 1893, **63**, 311.
d-Malic acid.	+3·0 (*c* = 5)	+ 16·2	+15·5 Stubbs, J., 1911, **99**, 2268.
d-Tartaric acid.	+21·3 (*c* = 5)	+ 59·9	+64·4 Landolt, *Ber.*, 1873, **6**, 1073.
l-Hexahydromandelic acid.	−21·3 (in alcohol)	+ 13·6	+ (ammonium) Wood and Comley, J., 1924, **125**, 2639.
l-Mandelic acid.	−240 (*c* = 1·6)	−179	—
d-β-Phenyl-lactic acid.	+38·0 (*c* = 2·7)	+ 79·5	+75·7 Clough.

TABLE II.

The Molecular Rotations of the Lower Esters of Some α-Hydroxy-acids.

		Methyl.	Ethyl.	*n*-Propyl.	*n*-Butyl.
l-Lactates.*	$[M]_D^{15°}$	+ 8·6°	+ 13·4°	+17·4°	+19·6°
l-Glycerates.†	$[M]_D^{15°}$	+ 5·8	+ 12·3	+19·1	+21·4
d-Malates.†	$[M]_D^{20°}$	+ 11·1	+ 19·3	+25·3	+26·4
d-Tartrates.†	$[M]_D^{20°}$	+ 3·7	+ 15·9	+29·7	+27·0
l-Hexahydromandelates.‡	$[M]_D^{20°}$	− 36·8	− 24·4	−15·5	−15·4
l-Mandelates.	$[M]_D^{20°}$	−276	−233	—	−209 (*iso*-)
d-β-Phenyl-lactates.§	$[M]_D^{20°}$	+ 8·5	+ 14·7 (at 17°)	—	—

* Wood, Such, and Scarf, J., 1923, **125**, 601. † For references, see Frankland and Gebhard, J., 1905, **87**, 865. ‡ Wood and Comley, *loc. cit.* § Clough; McKenzie and Barrow, J., 1911, **99**, 1021.

TABLE III.

The Molecular Rotations of the Amides of Some α-Hydroxy-acids.

	Methyl ester.	Amide.*
l-Lactic acid.	+ 8·6°	+ 19·6° (in water)
l-Glyceric acid	+ 5·8	+ 66·2 (in methyl alcohol)
d-Malic acid.	+ 11·1	+ 52·8 (in water)
d-Tartaric acid.	+ 3·7	+164 (in water)
l-Hexahydromandelic acid.	− 36·8 (at 30°)	+ 65·4 (in aqueous alcohol)
l-Mandelic acid.	−276	−144 (in water)
d-β-Phenyl-lactic acid.	+ 8·5	+104·2 (in ethyl alcohol) †

* For references, see Freudenberg, Brauns, and Siegel, *Ber.*, 1923, **56**, 195.
† McKenzie, Martin, and Rule, J., 1914, **105**, 1599.

From Table IV it is evident that acetylation of the methyl esters of the standard "*d*"-acids (except that of *d*-tartaric acid) causes the molecular rotations to increase. The introduction of one acetyl group into methyl *d*-tartrate raises the molecular rotation, but two acetyl groups in the molecule produce a depression in the molecular rotation. Acetylation of methyl *d*-β-phenyl-lactate is accompanied by an increase in the molecular rotation, but although methyl *l*-acetylmandelate possesses a higher specific rotation (− 146°) than methyl *l*-mandelate (− 166°), the molecular rotation of the former is lower than that of the latter compound. The molecular rotations of the benzoyl derivatives exhibit more irregularities; thus, the complete benzoylation of methyl *l*-lactate, of methyl *l*-glycerate, or of methyl *d*-tartrate produces decreases in the molecular rotations, but the introduction of one benzoyl group only into ethyl *d*-tartrate and the benzoylation of methyl *d*-malate are accompanied by increases in the molecular rotations. The values in Table IV show that an increase in the molecular (or the specific) rotation of methyl *d*-β-phenyl-lactate is produced on benzoylation and that an increase in specific rotation (but a decrease in molecular rotation) accompanies benzoylation of methyl *l*-mandelate. Whilst the data for the benzoyl derivatives do not confirm or refute the conclusions drawn respecting the relative configurations of *l*-mandelic and *d*-β-phenyl-lactic acids, the optical rotatory power of methyl *l*-phenylmethoxyacetate is in accordance with the view that *l*-mandelic acid is a "*d*"-α-hydroxy-acid.

TABLE IV.

The Molecular Rotations of the Acetyl, Benzoyl and Methyl Derivatives of Some α-Hydroxy-acids.

	Acetyl.	Benzoyl.	Methyl.
Methyl *l*-lactate (+8·6°).	+ 76·4°	− 35·6° *	+112·7°
Methyl *l*-glycerate (+5·8).	+ 24·6	− 87·5	+103·8
Methyl *d*-malate (+11·1).	+ 46·8	+ 15·0	+ 92·4
Methyl *d*-tartrate (+3·7).	+ 16·6 (mono-, in water)†	−280 (di-, at 100°)	+180·0
	− 39·6 (di-, in alcohol)		
Methyl *l*-mandelate (−276).	−304	−382 ‡	−173 (in acetone) §
Methyl *d*-β-phenyl-lactate (+8·5).	+ 16·3	+ 92·2 ‡	—

* Freudenberg and Rhino, *Ber.*, 1924, **57**, 1556. † Freudenberg and Brauns, *Ber.*, 1922, **55**, 1349. ‡ Clough. § McKenzie and Wren, J., 1910, **97**, 484.

It is worthy of note that the effect of a rise of temperature on the optical rotatory powers of the esters of *l*-hexahydromandelic acid (Wood and Comley, *loc. cit.*) is similar to that on the esters of *l*-lactic acid, *l*-glyceric acid, *d*-malic acid, *d*-tartaric acid, and

l-mandelic acid. The influence of organic solvents on optical rotatory power will be discussed by the author in a later paper.

The regularities observed in the influence of sodium, barium, and other halides on the optical rotatory powers of α-hydroxy-acids or their esters in solution have also been employed for determining the relative configurations of these optically active compounds. The data in Table V fully confirm the results already obtained. It should be pointed out that other inorganic compounds added to aqueous solutions of the acids in question do not always produce similar alterations in the rotatory powers. For example, boric acid produces a diminution in the optical rotatory power of *l*-(" *d* ")-lactic acid (Henderson and Prentice, J., 1902, **81**, 658), but causes an elevation of that of *d*-tartaric acid (Biot).

TABLE V.

The Influence of Sodium Bromide on the Optical Rotatory Powers of Some Esters of α-Hydroxy-acids in Methyl-alcoholic Solution.

	In methyl alcohol.	In methyl-alcoholic sodium bromide (*N*).
Methyl *d*-malate.	+ 8·7° (*c* = 5)	− 8·0° (*c* = 5)
Ethyl *d*-malate.	+ 11·6 (*c* = 5)	− 2·4 (*c* = 5)
Methyl *d*-tartrate.	+ 4·6 (*c* = 5)	− 8·4 (*c* = 5)
n-Propyl *d*-tartrate.	+ 16·0 (*c* = 5)	+ 2·6 (*c* = 5)
Methyl *l*-mandelate.	−142 (*c* = 3)	−172 (*c* = 3)
Ethyl *l*-mandelate.	−117 (*c* = 10)	−150 (*c* = 10)
Methyl *d*-β-phenyl-lactate.	− 2·4 (*c* = 2·7)	− 16·3 (*c* = 2·7)
Ethyl *d*-β-phenyl-lactate.	+ 0·8 (*c* = 5)	− 12·0 (*c* = 5)

That the principle employed in this investigation also leads to correct deductions in other classes of compounds is shown by Karrer's confirmation of the present author's view that *l*-asparagine, *l*-aspartic acid, and *l*-leucine are configuratively related to *d*-(" *l* ")-alanine (*Helv. Chim. Acta*, 1923, **6**, 957; see Part I, p. 539). Moreover, a study of the optical rotatory dispersive powers of a number of corresponding derivatives from the optically active α-amino- and α-hydroxy-propionic acids has revealed regularities from which Freudenberg and Rhino have drawn the conclusion that *l*-(" *d* ")-alanine possesses the same configuration as *l*-(" *d* ")-lactic acid (*Ber.*, 1924, **57**, 1551; see Part I, p. 548).

EXPERIMENTAL.

l-*Mandelic Acid.*—In water (*c* = 1·59): $\alpha^{14°}_{5893}$ (*l* = 2) − 5·03°, $\alpha^{14°}_{5780}$ − 5·28°, $\alpha^{14°}_{5461}$ − 5·98°, $\alpha^{14°}_{4078}$ − 13·55°; $[\alpha]^{14°}_{5893}$ − 158°, $[\alpha]^{14°}_{5780}$ − 166°, $[\alpha]^{14°}_{5461}$ − 188°, $[\alpha]^{14°}_{4078}$ − 426°.

In aqueous sodium chloride (4*N*) (*c* = 1·59): $\alpha^{14°}_{5461}$ (*l* = 2) − 6·45°; $[\alpha]^{14°}_{5}$ − 203°.

Ethyl l-*Mandelate.*—$d^{15°}_{4}$ 1·128; $\alpha^{15°}_{5893}$ (*l* = 0·5) − 73·04°, $\alpha^{15°}_{5780}$ − 76·55°, $\alpha^{15°}_{546}$ − 88·10°; $[\alpha]^{15°}_{5893}$ − 129·4°, $[\alpha]^{15°}_{5780}$ − 135·7°, $[\alpha]^{15°}_{5461}$ − 156·4°.

In methyl alcohol ($c = 10$) : $\alpha^{15^\circ}_{5893}$ ($l = 2$) $-$ 23·48°, $\alpha^{15^\circ}_{5780}$ $-$ 24·38°, $\alpha^{15^\circ}_{5461}$ $-$ 28·20°, $\alpha^{15^\circ}_{4073}$ $-$ 65·0°; $[\alpha]^{15^\circ}_{5893}$ $-$ 117·4°, $[\alpha]^{15^\circ}_{5780}$ $-$ 121·9°, $[\alpha]^{15^\circ}_{5461}$ $-$ 141·0°, $[\alpha]^{15^\circ}_{4078}$ $-$ 325°.

In methyl-alcoholic sodium bromide (N) ($c = 10{\cdot}12$) : $\alpha^{15^\circ}_{5893}$ ($l = 2$) $-$ 30·30°, $\alpha^{15^\circ}_{5461}$ $-$ 36·55°; $[\alpha]^{15^\circ}_{5893}$ $-$ 149·6°, $[\alpha]^{15^\circ}_{5461}$ $-$ 180·5°.

Methyl l-*phenylbenzoyloxyacetate*, prepared by the action of benzoyl chloride on methyl *l*-mandelate in presence of pyridine, boiled at 224—225°/18 mm.

$d^{20^\circ}_{4^\circ}$ 1·217; $\alpha^{20^\circ}_{D}$ ($l = 0{\cdot}5$) $-$ 86·05°; $[\alpha]^{20^\circ}_{D}$ $-$ 141·4°.

Methyl l-β-*phenyl-lactate* was prepared by McKenzie and Martin's method (J., 1913, **103**, 117).

$d^{20^\circ}_{4^\circ}$ 1·129; $\alpha^{20^\circ}_{D}$ ($l = 1$) $-$ 5·35°; $[\alpha]^{20^\circ}_{D}$ $-$ 4·74°.

Methyl d-α-*acetoxy*-β-*phenylpropionate*, m. p. 30—31°, b. p. 185°/20 mm., was prepared by the action of acetyl chloride on methyl *d*-β-phenyl-lactate in presence of pyridine.

$d^{18^\circ}_{4^\circ}$ 1·125; $\alpha^{18^\circ}_{D}$ ($l = 1$) + 8·23°; $[\alpha]^{18^\circ}_{D}$ + 7·33°.

Methyl l-α-*benzoyloxy*-β-*phenylpropionate*, b. p. 224—225°/16 mm., was prepared by the action of benzoyl chloride on methyl *l*-β-phenyl-lactate in presence of pyridine.

$d^{20^\circ}_{4^\circ}$ 1·161; $\alpha^{20^\circ}_{D}$ ($l = 1$) $-$ 37·65°; $[\alpha]^{20^\circ}_{D}$ $-$ 32·45°.

The above esters required the correct amounts of sodium hydroxide for complete saponification, which was unaccompanied by change of sign of rotation. Some racemisation may have occurred in the preparation of methyl *l*-phenylbenzoyloxyacetate; Freudenberg and Markert (*loc. cit.*) give $[\alpha]^{20^\circ}_{578}$ $-$ 159·9° for this compound.

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CCCLXXXVIII.—*The Action of Silica on Electrolytes. Part II.*

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THE action of silica on two classes of electrolytes—acids * and salts—has already been studied (Joseph and Hancock, J., 1923, **123**, 2022). Its effect on bases is now described. It must again be

* The experiments with acids have been repeated with purified "silica gel" with the same result. There has been some correspondence in *Nature* (Jan. 31st, March 28th, and April 4th) on this subject, but the present authors have not yet obtained experimental evidence requiring a change of opinion.

emphasised that a high degree of purity of the silica is essential for work of this kind, as the presence of a small quantity of basic impurity has an important effect on its properties. For example, a sample of silica gel which retained 6% of water after drying at 180° retained only 3·2% if it had been washed with hydrochloric acid (followed by water) before being dried.

Silicates of the Alkali and the Alkaline-earth Metals.—Many studies on these substances at high temperatures have been carried out in recent years, but data as to reactions taking place in presence of much water at the ordinary temperature are scanty. The following facts bear on what follows : Potassium seems to form silicates of greater stability in water and lower solubility than sodium : the properties of potash glass bear this out, and also the fact (Morey, *J. Amer. Chem. Soc.*, 1914, **36**, 230) that the compound $KHSi_2O_5$ may be left for hours with water at 100° without undergoing appreciable decomposition. Calcium silicate is less soluble in water than the barium salt. The sodium silicates, even when containing a high proportion of silica, are all acted on by water to a noticeable degree.

The equilibrium between silicic acid and sodium hydroxide was studied by constructing a titration curve for a " water glass " solution containing 2 mols. of silica to 1 mol. of sodium oxide. The first points on the curve were obtained by the addition of hydrochloric acid, and the later ones by the addition of sodium hydroxide. In each case the hydroxyl-ion concentration was determined by p_H measurement, and the amount of sodium silicate present was found by subtracting the quantities of hydrochloric acid and hydroxyl from the total sodium. The results are in Table I. If the sodium oxide neutralised is plotted against p_H, the curve shows a definite inflexion when the solution contains 2 mols. of neutralised sodium oxide to 1 mol. of silica. The p_H at which the ratio is half this is very nearly 10, and this corresponds to the value 10^{-10} for the first dissociation constant of silicic acid. The combination between the second molecule of sodium oxide takes place between p_H values of 11·6 and 12·6, indicating that the second dissociation constant of the acid is about 10^{-12}. The curve is typical of the combination of a strong base with a weak dibasic acid.

TABLE I.

Solution contains 0·0186 mol. of silica per litre.

p_H	3·2	9·40	9·90	10·0 *	10·72
Mols. Na_2O neutralised...	0·0	0·0017	0·0043	0·0046 *	0·0086
p_H	11·77	12·28	12·31	12·53	12·63
Mols. Na_2O neutralised...	0·0112	0·0180	0·0278	0·0745	0·1570

The point marked * was obtained by interpolation.

The Action of Alkaline Hydroxides on Silica.—When pure silica is acted on by an alkaline hydroxide, neutralisation of the base commences immediately, and the extent to which the reaction proceeds is dependent on the nature and the concentration of the base, the quantity of silica (at the surface of which the reaction takes place), as well as on the usual factors such as time of contact and temperature. The fineness of the silica will of course determine the amount of reactive surface, so that different specimens will not necessarily give the same quantitative results, although different series will be comparable amongst themselves.

The immediate effect is the production of a silicate at the surface of the silica. This is followed by its partial dissolution caused by the solvent and hydrolytic action of the water. After a time, equilibrium is approached between the silicate in the solid and that in the liquid phase. Increase of concentration of either of the reagents causes an increase in the amount of silicate in each phase.

For equal concentrations of different bases, the amount of solid silicate formed depends on the solubility relationships of the silicate of the base used, being great where the solubility is small (as in the case of calcium) and small where the solubility is large (as in the case of sodium).

These statements are illustrated by the results tabulated below. The amount of silica taken is given as g. per 100 c.c. : in all other cases, concentrations are expressed as g.-equiv. per litre.

The silica was purified, and the p_H measurements were made, as previously described. The reactions were carried out in wax-coated glass flasks. The amount of hydroxyl-ion remaining in solution was calculated from the p_H measurements by means of the values of Michaelis for $1/\log K_w$ at the temperatures at which the experiments were made : these varied between 33° and 38°. From the hydroxyl-ion concentration, the concentration of free base was calculated from its known degree of dissociation at the working concentration.

Titration with standard hydrochloric acid gave the concentration in solution of the free base plus soluble silicate, and this, subtracted from the amount of base taken, gave the amount of the base retained in the solid phase. Neither thermostats nor shakers were used in this work.

TABLE II.

Effect of time on the progress of the reaction.

Silica 0·5%. Base 0·0365*N*.

Time	20 hours	48 hours	70 hours	12 days
% NaOH neutralised	53	63	86	94
% $Ca(OH)_2$ neutralised	68	79	98	99

See errata V. 1926 p. 3361

Table III.

Comparison of the amounts of solid silicate formed from different bases after 1 day. Initial concentration of base 0·405*N*.

Base.	Base neut.	Fraction of base neutr.	Solid silicate per litre.	Silicate in soln.	Solid as % of total.
NaOH	0·027	0·66	0·0014	0·026	5·2
KOH	0·029	0·71	0·0019	0·027	6·5
$Ba(OH)_2$	0·021	0·54	0·0063	0·014	30
$Ca(OH)_2$	0·034	0·84	0·034	0·000	100

The results follow the solubility relationships of the silicates of these four bases.

The barium experiment was made at a different time, and the initial concentration of the base was 0·0392.

Table IV.

Effect of the concentration of the base on the amounts of silicate formed in the solid and liquid phases after 2 days.

Initial NaOH.	Final NaOH.	Total silicate.	Solid silicate.	Silicate in soln.
0·004	0·00016	0·0038	Small	0·0038
0·014	0·00058	0·0134	0·00024	0·0132
0·030	0·00159	0·0285	0·00032	0·0282
0·060	0·00828	0·0515	0·00112	0·0504

Table V.

Effect of the amount of silica taken on that of the silicates formed in the solid and liquid phases after 8 days.

Base.	NaOH, 0·040*N*.		KOH, 0·040*N*.			$Ba(OH)_2$, 0·039*N*.		$Ca(OH)_2$, 0·038*N*.	
% Silica taken.	0·5	1·0	0·5	1·0	2·0	0·5	1·0	0·5	1·0
Solid silicate	0·0014	0·0027	0·0011	0·0021	0·0047	0·0063	0·0138	0·0349	0·0351
Silicate in soln.	0·0366	0·0369	0·0379	0·0383	0·0358	0·0054	0·0092	0·0028	0·0027
% Base neutr.	94	97	97	100	100	30	58	99	99

(*Note*.—The experiments with sodium hydroxide were carried out with a different specimen of silica : this does not affect the relationships which the above table is designed to show.)

From the above two tables it appears that there is (*a*) a direct equilibrium between solid silica, solid silicate and liquid phase (hydroxide and silicate in solution) which is the main factor in the case of sodium and potassium; and (*b*) an ordinary solubility relationship between solid and soluble silicates which is the main factor where, as in the case of calcium and barium, no easily soluble silicates exist. It follows from (*a*) that any reduction in the

amount of free silica should be accompanied by a reduction in the amount of solid silicate, and this is shown by the following figures for the time effect of a stronger solution of sodium hydroxide on silica: the gradual passage into solution of the silica is accompanied by a fall in the amount of solid silicate.

TABLE VI.

Simultaneous disappearance into solution of silica and solid silicate. 1% Silica = 0·167 mol. per litre. NaOH, 0·0101*N*.

Time.	p_H.	Total silicate.	Solid silicate per litre.
5 hours	11·94	0·0768	0·0057
1 day	11·41	0·0937	0·0046
2 days	11·15	0·0972	0·0040
4 „	11·00	0·0981	0·0039
8 „	10·93	0·0986	0·0037

Effect of Neutral Salts on the Reaction.—The reactions between neutral salts and silica have been dealt with in the previous paper: acidity is always developed and some of the base goes into the solid phase. The addition of a salt to a mixture of silica and alkali should favour the formation of insoluble silicate by depressing the solvent and hydrolytic action of the water, and this is found to be the case. Table VII gives the results of parallel experiments carried out with and without the addition of the chloride of the base concerned.

TABLE VII.

1% Silica and 0·04*N*-base. Time of standing, 1 day. Conc. of salt soln. = *N*.

Fraction of added base found in solid phase.

Base.	Without salt.	With salt.
NaOH	0·030	0·078
KOH	0·035	0·149
$Ca(OH)_2$	0·70	0·85
$Ba(OH)_2$	0·161	0·210

Experiments carried out with sodium chloride and different amounts of silica showed that, as before, the amount of silica determined that of the solid silicate formed (which is, of course, very small in the absence of free base). Titration methods could not be applied, but the hydrogen ions liberated were equivalent to the solid silicate, and this is seen to be roughly proportional to the silica taken.

TABLE VIII

Silica taken.	p_H of mixture.	H-ion conc.
1%	4·01	0·00010
2%	3·74	0·00018

Summary.

(*a*) The action of an alkaline hydroxide on silica results in the formation of a solid silicate, part of which passes into solution. The amount of solid silicate formed is very small with sodium and potassium, about 50% in the case of barium, and nearly 100% with calcium. These results are in accordance with the solubilities of the silicates of these bases.

(*b*) In the case of sodium and potassium, the small amount of solid silicate produced is roughly proportional to the weight of silica taken, although the amount of silicate in solution is only slightly affected. These relationships show that the solid phases (silica and silicate) are directly concerned in the equilibrium.

(*c*) The addition of a neutral salt increases considerably the amount of solid silicate produced.

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CCCLXXXIX.—*Isomeric Change in Aromatic Compounds. Part I. The Conversion of Diacylanilides into Acylamino-ketones.*

By ARTHUR WILLIAM CHAPMAN.

IN the course of an investigation on imino-aryl ethers it was found that when a current of dry hydrogen chloride was passed through fused dibenzanilide at 250—270° benzoyl chloride and benzanilide were produced:

$$PhN(COPh)_2 + HCl = PhNH{\cdot}COPh + PhCOCl.$$

Diacetanilide decomposed in a similar manner, yielding at 150—170° acetyl chloride and acetanilide.

Diacylanilides, when heated in presence of either hydrogen chloride or zinc chloride, are converted into the corresponding acylamino-ketones by what has been regarded as an intramolecular change (Chattaway and Lewis, J., 1904, **85**, 386, 589, 1663; Angel, J., 1912, **101**, 515; Derick and Bornmann, *J. Amer. Chem. Soc.*, 1913, **35**, 1269). Migration does not occur in the absence of a catalyst of this kind, and the necessary conditions are exactly those under which hydrogen chloride decomposes the diacylanilides. It seems, then, more reasonable to suppose that, with hydrogen chloride as catalyst, the change takes place by decomposition of the diacylanilide into acyl chloride and anilide and recondensation to yield the ketone and hydrogen chloride:

$$C_6H_5{\cdot}NAc_2 + HCl \rightarrow C_6H_5{\cdot}NHAc + AcCl \rightarrow C_6H_4Ac{\cdot}NHAc + HCl.$$

Zinc chloride, especially if it has been allowed to become damp, usually contains a little free hydrogen chloride, and this would account for its catalytic activity. Diacetanilide remained almost unchanged when heated at 140—160° in presence of dry zinc chloride alone, but was readily converted into *p*-acetylaminoacetophenone when hydrogen chloride was passed into the mixture. The hydrogen chloride therefore appeared to be the essential factor, although the zinc chloride no doubt assisted by acting as a condensing agent in the second stage of the conversion.

The conversion of diacylanilides into acylamino-ketones furnishes yet another example of the numerous isomeric changes in the aromatic series which have been shown to proceed by fission of the mobile group followed by recondensation, such as the Hofmann–Martius change (Beckmann and Correns, *Ber.*, 1922, **55**, 852), the Fischer–Hepp change (O. Fischer, *Annalen*, 1895, **286**, 145), the conversion of phenolic esters into hydroxy-ketones (Skraup and Poller, *Ber.*, 1924, **57**, 2033), and the isomeric change of imino-aryl ether hydrochlorides (J., 1922, **121**, 1676; 1923, **123**, 1150).

It is proposed to extend the present study to other similar isomeric changes which have not yet been investigated from this point of view.

Experimental.

Decomposition of Dibenzanilide and of Diacetanilide by Hydrogen Chloride.—Dry hydrogen chloride was passed through the fused diacylanilide, the temperature of which was gradually raised until distillation began and was then maintained constant until no more liquid came over.

Diacetanilide (20 g.) yielded a colourless distillate (6·7 g.), b. p. 51—53°, which reacted with *p*-toluidine to give aceto-*p*-toluidide (m. p. 147°). The residue (11·5 g.), b. p. 286—290°, crystallised from benzene or water in shining leaves (m. p. 114°, alone or mixed with acetanilide).

p-Aminoacetophenone, *p*-acetylaminoacetophenone and acetanilide did not yield any acetyl chloride on treatment with hydrogen chloride even at 200—250°.

Dibenzanilide (10 g.) yielded benzoyl chloride (2·1 g.; b. p. 193—200°; converted by phenol and sodium hydroxide into phenyl benzoate, m. p. 68—69°) and benzanilide (4·8 g.; m. p. after recrystallisation 159—160°, not depressed by admixture with an authentic specimen).

Conversion of Diacetanilide into p-*Acetylaminoacetophenone.*—A mixture of diacetanilide (20 g.) and powdered dry zinc chloride (3 g.) was heated at 140—160° while hydrogen chloride was led into

it for 4½ hours. Since *p*-acetylaminoacetophenone is difficult to isolate as such, the product was hydrolysed by boiling with concentrated hydrochloric acid (150 c.c.) and the solution was made alkaline with solid sodium hydroxide, steam-distilled to remove aniline, cooled, and filtered. Boiling light petroleum extracted from the precipitate about 2 g. of *p*-aminoacetophenone (m. p. 106—107°, not depressed by admixture with an authentic sample).

In a similar experiment without hydrogen chloride, no *p*-aminoacetophenone was isolated from the light petroleum extract, but the alkaline aqueous liquor gave a deep red dye on diazotisation and coupling with β-naphthol. In two control experiments in which diacetanilide was heated alone, no *p*-aminoacetophenone could be detected even by the diazo-reaction.

p-Aminoacetophenone was also obtained by passing acetyl chloride vapour through fused acetanilide and zinc chloride, but was accompanied by much diphenylethenylamidine (m. p. 132—133°), formed by the condensation of 2 mols. of acetanilide with elimination of acetic acid.

THE UNIVERSITY, SHEFFIELD. [*Received, October 14th*, 1925.]

CCCXC.—*The Partial Pressures of Water Vapour and of Sulphuric Acid Vapour over Concentrated Solutions of Sulphuric Acid at High Temperatures.*

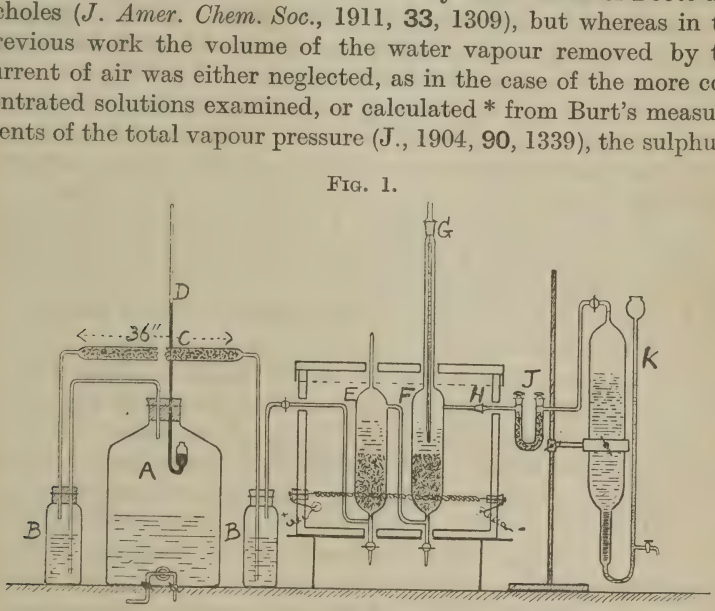
By JOHN SMEATH THOMAS and WILLIAM FRANCIS BARKER.

THIS investigation was undertaken with the object of extending the measurements of Thomas and Ramsay (J., 1923, **123**, 3256). These authors determined the partial pressures of the sulphuric acid only. It seemed desirable also to obtain data regarding the partial pressures of the water vapour in equilibrium with concentrated solutions of the acid over the same range of temperature.

At an early stage in the work it became evident that the results obtained in the previous investigation were uniformly low. Further examination revealed two sources of error: (*a*) adsorption of sulphuric acid vapour on the glass wool employed to remove "mist," and (*b*) the possibility that the liquid was not in thermal equilibrium with the heating bath. Of these, the former is the more serious; it had been foreseen, but the precautions taken against it now appear to have been inadequate. As regards the second possibility, in the previous work the actual temperature of the acid was not measured; it was assumed to have attained the temperature of the bath, considerable time having been allowed for this purpose.

In this investigation, the apparatus was modified to eliminate these errors as far as possible, and measurements of the partial pressures of the water vapour and of the sulphuric acid were made at a series of temperatures ranging from 180° to 300°. The dynamical method (*loc. cit.*) was again employed, the partial pressures being calculated from the experimental data by the method of Foote and Scholes (*J. Amer. Chem. Soc.*, 1911, **33**, 1309), but whereas in the previous work the volume of the water vapour removed by the current of air was either neglected, as in the case of the more concentrated solutions examined, or calculated * from Burt's measurements of the total vapour pressure (J., 1904, **90**, 1339), the sulphuric

FIG. 1.



acid partial pressures of these more dilute solutions being assumed to be negligible, in the present work it was obtained from the actual weight of water removed by the air. The partial pressure is then given by the formula

$$p = 760\ v/(v_1 - v_2),$$

in which v represents the volume of the water vapour or the sulphuric acid vapour as the case may be, v_1 the volume of air (reduced to N.T.P.), and v_2 the combined volumes of the water vapour and the sulphuric acid vapour removed during the experiment. In calculating these volumes the value 22·3 litres was taken for the gram-molecular volume.

EXPERIMENTAL.

The modifications in the apparatus can best be understood by reference to Fig. 1.

* In the previous communication reference to this correction for the volume of the water vapour was inadvertently omitted.

A current of air from the aspirator A was dried and freed from carbon dioxide by passing it through the vessels B and C, containing concentrated sulphuric acid and soda-lime, respectively. The aspirator was fitted with the manometer D in order that the air supply might be kept at constant pressure—a pressure equivalent to 900 mm. Hg was found to be convenient. This greatly facilitated the experimental manipulation of the apparatus. From C, the dried and purified air passed through the saturators E and F, which contained the acid solution under investigation.

These saturators, each having a working capacity of approximately 250 c.c., were constructed and arranged in the thermostat in the manner indicated in the diagram. They were half filled with short pieces of glass tube of narrow bore and worked very efficiently; the tiny air bubbles produced by the constricted vertical air inlet tube followed a circuitous path and remained in contact with the acid for a considerable time. From the bottoms of the saturators vertical tubes passed through the bottom of the thermostat and to these taps were sealed, by means of which acid was introduced and specimens could be withdrawn for analysis. To the upper portion of the final saturator a wide glass tube was sealed; a thermometer, fitted into this by means of the ground joint, G., dipped below the surface of the acid, the actual temperature of which could thus be observed. Although no regulator was used, this temperature remained very constant; variations in the voltage of the electrical supply occasionally gave rise to slight changes. During an experiment the temperature was observed at 2-minute intervals. These readings were plotted and from the graph the mean temperature was obtained.

The thermostat consisted of a double-walled box, the outer wall being of galvanised iron and the inner wall, which was separated from the outer by an air space of about $\frac{1}{2}$ inch, of asbestos slate. Through each side of the box two insulated terminals passed, leading to the heating units—spirals of nichrome wire—any of which could be used or cut out at will, according to the temperature required. The final temperature regulation was effected by means of an adjustable external resistance.

The air, saturated with acid vapour, passed from the final saturator through the absorbing vessels, J, into the measuring device, K. Two of these vessels were employed, but only one is shown in the diagram. Each had a capacity of about 300 c.c.; the volume between the fixed marks had been carefully determined and the lower limb was graduated. During the experiment water was run out at such a rate as to keep the air under atmospheric pressure.

Each experiment involved two determinations: (*a*) the total

weight of vapour (sulphuric acid and water) removed by a given volume of air, and (*b*) the weight of the removed sulphuric acid vapour alone. For the determination of the total weight of vapour a series of absorption tubes was used. These contained solid sodium hydroxide followed by granular calcium chloride and were carefully weighed before and after each experiment with all the usual precautions. For the estimation of the sulphuric acid vapour the conductivity method described (*loc. cit.*) was employed, except in the case of the 99·23% solution; no water vapour could be detected in the vapour from this and the increase in weight of the absorption tubes was assumed to be entirely due to sulphuric acid.

Connexion between the absorbing vessels and the final saturator was made by means of the carefully ground joint, H, which was situated inside the thermostat, thus obviating the premature condensation of vapour. The inner portion of this joint projected into a small bulb, not shown in the diagram, the object of which was to prevent the creeping of acid along the surface of the glass into the absorbing vessels.

Preliminary experiments having disclosed that the use of glass wool for the prevention of the mechanical transference of acid in the form of "mist" leads to serious errors, this end was attained by using an extremely slow current of air; in the final experiments the rate of flow never exceeded 150 c.c. per hour. On examining the brightly illuminated space above the surface of the acid, no trace of mist could be seen.

The strength of the various acid solutions examined was determined gravimetrically. Analysis of four samples from each saturator at the close of the series of determinations revealed no change in concentration.

The Variation of the Partial Pressures with the Temperature.

Five series of measurements were made on sulphuric acid solutions of concentrations between 89·25 and 99·23% H_2SO_4, in each case at a number of different temperatures ranging from 180° to 295°; on account of the lower boiling points of the more dilute solutions measurements could not be made at the higher temperature. The results are in Table I, in which the pressures are expressed in mm. of mercury.

In calculating the values in columns 2, 3, and 4 the assumption has been made that the sulphuric acid vapour is not dissociated, whilst the values in the next three columns are based on the assumption that complete dissociation of the acid vapour occurs. The values for the dissociated acid cannot be obtained from the corresponding figures for undissociated acid by means of the expres-

TABLE I.

t.	$p_{H_2SO_4}$.	p_{H_2O}.	P.	Assuming complete dissociation. p'_{SO_3}.	p'_{H_2O}.	P'.
			Series A. 89·25% H_2SO_4.			
183·0°	0·5	78·8	79·3	0·5	79·2	79·7
197·5	1·3	116·9	118·2	1·3	118·0	119·3
216·5	2·1	233·1	235·2	2·1	234·6	236·7
230·0	3·6	306·3	309·9	3·6	308·4	312·0
241·5	5·3	414·8	420·1	5·3	417·2	422·5
			Series B. 91·26% H_2SO_4			
191·0	0·6	50·7	51·3	0·6	51·3	51·9
205·0	1·9	84·7	86·6	1·9	86·1	88·0
222·0	4·5	158·5	163·0	4·5	162·1	166·6
242·5	6·4	271·6	278·0	6·4	275·7	282·1
252·5	11·3	385·3	396·6	11·1	390·7	401·8
258·0	13·6	448·7	462·3	13·4	454·2	467·6
262·5	16·3	411·1	427·4	15·9	419·0	434·9
			Series C. 95·06% H_2SO_4.			
180·0	2·1	10·1	12·2	2·1	12·2	14·3
200·0	4·8	21·2	26·0	4·8	25·8	30·6
215·5	8·5	46·5	55·0	8·4	54·4	62·8
232·0	13·4	91·9	105·3	13·2	103·5	116·7
244·5	19·9	120·1	140·0	19·4	136·4	155·8
252·0	20·0	156·5	176·5	19·5	172·0	191·5
261·0	27·9	180·7	208·6	26·9	201·1	228·0
270·0	39·9	254·9	294·8	37·8	279·6	317·4
280·5	52·0	310·0	362·0	48·7	351·9	400·6
282·0	52·6	350·2	402·8	49·2	376·5	425·7
			Series D. 98·06% H_2SO_4.			
204·0	5·9	0·0	5·9	5·9	5·9	11·8
218·5	9·8	1·5	11·3	9·7	11·2	20·9
234·5	14·7	3·2	17·9	14·4	17·6	32·0
249·0	28·5	2·6	31·1	27·5	30·0	57·5
261·0	38·8	5·0	43·8	36·9	41·6	78·5
273·0	61·9	5·3	67·2	57·2	62·5	119·7
285·0	91·6	11·8	103·4	81·8	92·2	174·0
295·0	132·3	14·7	147·0	112·7	125·2	237·9
			Series E. 99·23% H_2SO_4.			
211·0	33·2	—	33·2	33·2	33·2	66·4
225·0	49·9	—	49·9	49·9	49·9	99·8
227·0	55·4	—	55·4	55·4	55·4	110·8
244·0	84·1	—	84·1	84·1	84·1	168·2
261·0	163·8	—	163·8	163·8	163·8	327·6
270·0	229·8	—	229·8	229·8	229·8	459·6
281·0	272·3	—	272·3	272·3	272·3	544·6
290·0	381·5	—	381·5	381·5	381·5	763·0

sions $p_{H_2SO_4} = p'_{SO_3}$ and $P'_{diss.} = 2p_{H_2SO_4} + p_{H_2O}$, where p' refers to acid in which dissociation is assumed. The reason for this lies in the method, which is applicable whichever assumption is made, but which does not allow of results being translated from one basis to the other because of the volume change which must be taken into account. The following example, taken from an actual experi-

ment on 91·26% H_2SO_4, makes this point clear. In this example the question is simplified because the volume of air used in the two runs chanced to be the same. 292·3 C.c. of air at *N.T.P.* were passed through the acid (262·5°). The increase in weight of the absorption tubes was 0·3554 g. and the weight of acid absorbed in conductivity water was 0·0630 g. *Assuming no dissociation*: Vol. of 0·0630 g. H_2SO_4 and 0·2924 g. H_2O at *N.T.P.* = 14·3 and 362·2 c.c., respectively. Total vol. = 668·8 c.c. $p_{H_2SO_4} = 14·3 \times 760/668·8 = 16·3$ mm. and $p_{H_2O} = 362·2 \times 760/668·8 = 411·1$ mm. Therefore $P = 427·4$ mm. *Assuming the acid to be completely dissociated*: Weight of SO_3 in the acid vapour removed = $0·0630 \times 80/98 = 0·0514$ g., and weight of water removed = $0·3554 - 0·0514 = 0·3040$ g. The corresponding volumes at *N.T.P.* are 14·3 and 376·6 c.c., respectively. Total volume = 683·2 c.c. $p'_{SO_3} = 14·3 \times 760/683·2 = 15·91$ mm. and $p'_{H_2O} = 376·6 \times 760/683·2 = 419·0$ mm. Therefore $P'_{diss.} = 434·91$ mm. But $2p_{H_2SO_4} + p_{H_2O} = 443·7$ mm. The difference between the results obtained by the two methods of calculation is not serious for the more dilute acids at moderate temperatures. It becomes important at higher temperatures, especially when the concentration exceeds 95%.

Although, for the sake of uniformity, all the experimental results are carried to the first decimal place, this degree of accuracy is not necessarily claimed for each single determination.

At low temperatures the relation between temperature and partial pressure of the water or of the acid vapour was approximately linear in both cases. At higher temperatures, however, the partial pressures increase, with increasing temperature, more rapidly than this simple relationship demands. The variation of the partial pressure with change of temperature can be represented with considerable accuracy by expressions such as that used by Perman for solutions of ammonia in water, or better, by Rankine's equation $\log_{10} p = \alpha - \beta/T - \gamma \log T$. The constants α, β, and γ, in the latter expression were obtained in the usual way from values taken from the smoothed curve.

99·23% H_2SO_4	p	$\alpha = -20·0946$;	$\beta = 1695·86$;	$\gamma = -9·3427$.
98·06% H_2SO_4	$p_{H_2SO_4}$	$\alpha = 8·2878$;	$\beta = 4319·7$;	$\gamma = -0·5166$.
	p_{H_2O}	$\alpha = 20·7109$;	$\beta = 5415·31$;	$\gamma = 3·6353$.
	P	$\alpha = 10·8170$;	$\beta = 4518·21$;	$\gamma = 0·2571$.
95·06% H_2SO_4	$p_{H_2SO_4}$	$\alpha = -106·5692$;	$\beta = -4828·25$;	$\gamma = -36·2945$.
	p_{H_2O}	$\alpha = 22·4406$;	$\beta = 4541·0$;	$\gamma = 4·2726$.
	P	$\alpha = 8·4658$;	$\beta = 3516·97$;	$\gamma = -0·1707$.
91·26% H_2SO_4	$p_{H_2SO_4}$	$\alpha = 48·2388$;	$\beta = 7026·67$;	$\gamma = 12·4310$.
	p_{H_2O}	$\alpha = 65·2394$;	$\beta = 7354·24$;	$\gamma = 17·8856$.
	P	$\alpha = 66·8040$;	$\beta = 7483·28$;	$\gamma = 18·3659$.
89·25% H_2SO_4	$p_{H_2SO_4}$	$\alpha = 75·5303$;	$\beta = 8529·90$;	$\gamma = 21·4699$.
	p_{H_2O}	$\alpha = -32·5120$;	$\beta = 216·85$;	$\gamma = -13·114$.
	P	$\alpha = -33·5235$;	$\beta = 155·653$;	$\gamma = -13·4453$.

TABLE II

	99·23% H_2SO_4.			98·06% H_2SO_4.				
	$p_{H_2SO_4}$.	$p_{H_2SO_4}$.		$p_{H_2SO_4}$.	$p_{H_2SO_4}$.	p_{H_2O}.	p_{H_2O}.	
t.	obs.	calc.	P.	obs.	calc.	obs.	calc.	P.
180°	10·0	9·5	19·5	1·5	1·3	0·14	0·12	3·2
185	12·0	11·7	24·0	2·0	1·7	0·18	0·16	4·2
190	14·2	14·0	28·0	2·6	2·2	0·25	0·21	5·1
195	17·2	16·95	34·2	3·2	2·7	0·30	0·27	5·5
200	21·0	20·5	41·0	4·0	3·45	0·35	0·35	8·0
205	24·5	24·6	48·0	4·7	4·3	0·45	0·44	9·7
210	29·0	29·5	58·2	6·2	5·4	0·57	0·55	12·0
215	34·2	35·3	68·5	7·5	6·7	0·72	0·69	15·0
220	41·0	42·1	81·0	8·7	8·3	0·90	0·87	18·2
225	49·0	50·0	94·5	10·5	10·2	1·10	1·07	22·0
230	58·0	60·1	110·5	13·0	12·5	1·32	1·30	27·0
235	67·5	70·6	128·0	15·7	15·3	1·67	1·64	32·7
240	80·0	83·1	149·7	18·7	18·6	2·00	2·01	39·2
245	94·0	97·7	173·0	22·5	22·2	2·40	2·45	46·7
250	111·0	115·5	198·2	27·0	27·1	2·95	2·98	56·0
255	131·0	134·5	227·0	32·2	32·6	3·52	3·61	66·7
260	153·0	158·0	257·5	38·5	39·2	4·22	4·35	78·7
265	179·0	184·3	291·0	46·2	46·7	5·10	5·20	92·5
270	209·5	214·9	327·5	55·5	55·6	5·15	6·25	109·0
275	243·0	250·5	368·0	66·0	66·1	7·42	7·46	127·5
280	282·2	286·6	412·0	78·5	78·1	8·85	8·94	150·2
285	328·0	326·6	459·0	92·7	92·3	10·52	10·50	175·5
290	380·0	389·1	500·2	109·5	109·1	12·47	12·40	205·0
295	440·0	448·4	565·5	130·7	132·7	14·65	14·60	240·5
300	505·2	517·2	626·2	150·1	151·7	17·10	17·12	284·0
305	577·0	596·2	692·0	174·5	174·2	19·95	20·02	336·5
310	659·5	684·7	—	203·5	202·8	23·0	23·35	393·5
315	752·0	—	—	235·0	235·5	26·45	27·14	456·0
320	—	785·1	—	270·0	272·7	30·25	31·50	515·0

	95·06% H_2SO_4.					91·26% H_2SO_4.				
	$p_{H_2SO_4}$.	$p_{H_2SO_4}$.	p_{H_2O}.	p_{H_2O}.		$p_{H_2SO_4}$.	$p_{H_2SO_4}$.	p_{H_2O}.	p_{H_2O}.	
t.	obs.	calc.	obs.	calc.	P.	obs.	calc.	obs.	calc.	P.
180°	3·2	3·1	11·0	11·7	16·4	0·47	0·51	33·5	31·6	35·0
185	3·5	3·5	12·5	14·3	18·2	0·62	0·66	41·0	39·0	42·0
190	4·0	4·0	16·5	17·5	22·0	0·82	0·84	48·5	49·0	50·0
195	4·5	4·6	20·5	21·3	27·2	1·05	1·07	59·0	58·4	61·2
200	5·1	5·2	25·5	25·8	31·7	1·35	1·35	70·0	70·7	78·1
205	5·9	6·0	31·0	31·1	38·5	1·71	1·70	85·4	85·4	88·0
210	6·7	6·8	37·0	37·3	46·2	2·14	2·13	102·6	102·6	106·2
215	7·7	1·9	44·0	44·5	55·0	2·65	2·63	122·0	120·4	127·2
220	9·1	9·1	53·0	53·0	66·0	3·27	3·24	146·2	144·3	152·0
225	10·3	10·4	62·2	62·5	79·1	3·98	3·98	172·0	170·4	179·5
230	11·9	12·0	74·0	74·1	93·5	4·85	4·84	200·9	199·2	209·5
235	13·7	13·8	87·0	87·2	110·5	5·87	5·88	233·0	233·0	244·0
240	15·6	15·9	102·2	102·1	130·0	7·07	7·12	271·0	270·6	283·0
245	18·1	18·4	119·5	119·4	152·3	8·55	8·55	313·0	312·1	327·0
250	20·9	21·2	139·0	139·0	176·0	10·25	10·22	360·5	360·1	377·2
255	24·3	24·4	160·2	161·3	202·5	12·25	12·16	413·0	413·0	433·5
260	28·1	28·3	185·2	186·5	231·0	14·60	14·45	469·2	470·8	499·5
265	32·5	32·6	213·5	215·0	263·2	17·30	17·01	532·5	535·5	561·2
270	37·9	38·0	245·0	247·1	300·0	20·30	20·02	600·0	604·5	636·5
275	43·6	43·9	281·7	282·3	343·0	24·9	22·42	675·2	684·9	721·0
280	50·2	50·7	323·0	323·8	393·0					
285	58·0	58·4	369·0	369·4	452·2					
290	67·5	67·9	420·0	420·2	522·0					
295	78·5	78·4	478·0	476·3	600·0					
300	91·5	90·7	539·5	538·6	690·0					
305	106·5	105·7	608·0	607·7	—					

TABLE II (*continued*).

89·25% H_2SO_4.

t.	$p_{H_2SO_4}$ obs.	$p_{H_2SO_4}$ calc.	p_{H_2O} obs.	p_{H_2O} calc.	*P.*	*t.*	$p_{H_2SO_4}$ obs.	$p_{H_2SO_4}$ calc.	p_{H_2O} obs.	p_{H_2O} calc.	*P.*
180°	0·45	0·47	69·9	69·4	70·7	225°	3·07	3·12	263·7	265·5	268·0
185	0·60	0·60	82·5	78·8	83·5	230	3·67	3·71	303·0	306·0	307·9
190	0·75	0·75	96·0	94·7	97·3	235	4·34	4·42	347·0	348·9	353·2
195	0·95	0·94	111·7	110·3	113·2	240	5·10	5·22	400·0	403·2	408·0
200	1·18	1·17	128·1	128·4	131·0	245	6·00	6·13	463·0	462·8	471·2
205	1·43	1·44	149·5	148·7	160·9	250	7·13	7·16	534·1	530·0	545·0
210	1·75	1·76	172·0	172·2	174·8	255	8·25	8·35	614·0	605·0	628·5
215	2·12	2·15	198·5	199·4	201·7	260	9·56	9·66	702·0	691·5	723·5
220	2·56	2·59	229·5	230·0	235·5						

The values of the partial pressures and also of the total pressures taken from the smoothed curve, which may be looked upon as the true experimentally determined values, agree closely with the values calculated by means of these equations over the whole range. As was to be expected, the divergences are greatest at low temperatures. The observed and the calculated values of the partial pressures are set out in Table II. The values of *P* are obtained from the observed values on the assumption that the acid vapour undergoes complete dissociation.

On extrapolating the total-pressure curves to 760 mm. the boiling points of the different solutions are obtained.

Data concerning the boiling points of concentrated solutions of sulphuric acid have been given by Marignac (see "Sulphuric Acid and Sulphur Dioxide," Wyld, p. 194) and Beckmann (*Z. physikal. Chem.*, 1905, **53**, 129). The values obtained in this investigation are in good agreement with those obtained by graphical interpolation from the above-mentioned sources. They are shown in Table III.

TABLE III.

Conc. of acid.	B. p. from V. P. curve.	B. p. calc. from equation.	B. p. from other data.	$p_{H_2SO_4}$ at b. p. (mm.).	p_{H_2O} at b. p. (mm.).	B. p. calc. assuming H_2SO_4 vapour dissociated.
99·23%	315·2°	313·8°	310°	—	—	309·75°
98·06	349	352·8	331—338*	678·7	81·3	332·5
95·06	307·5	307·6	300	115	645	302·5
91·26	278·0	278·1	268·7	26·5	733·5	277
89·25	261·5	263·2	257	12·9	747·1	261

* The value 331·7° given by Landolt and Bornstein ("Tabellen," 5th ed., p. 1433) on the authority of Beckmann for the boiling point of pure sulphuric acid clearly should refer to the constant-boiling mixture containing 98·3% H_2SO_4.

In columns 5 and 6 of the above table are given the partial pressures of the water vapour and of the sulphuric acid vapour respectively at the boiling point.

Throughout this work it has been assumed that the sulphuric acid vapour remains undissociated. Whilst this may be approximately true at the lower temperatures, and especially for the more dilute solutions, the vapour in equilibrium with which always contains a large excess of water molecules, at higher temperatures, particularly in the case of the more concentrated solutions, this assumption cannot be justified. According to Dittmar (*Chem. News*, 1870, **20**, 258) pure sulphuric acid in the state of vapour is practically completely dissociated. If this is so, the values obtained for the sulphuric acid partial pressure will be lower than the real partial pressure of the dissociated acid, and the boiling points obtained from these measurements will therefore be too high. The figures given in Table III show this to be the case, although it should be pointed out that this influence, even supposing it to exert its maximum possible effect, is comparatively slight for solutions the concentrations of which lie below 95% H_2SO_4. For example, whereas complete dissociation of the sulphuric acid vapour would increase the total vapour pressure of 98·06% acid at 275° from 73·4 mm. to 127·5 mm., an increase of 73·7%, in the case of 91·26% H_2SO_4 the increase, at the same temperature, amounts to 3% only.

Unfortunately, the extent to which sulphuric acid vapour is dissociated at different temperatures and in the presence of widely varying concentrations of water vapour is not known and, consequently, no systematic correction for this factor can be applied to the values obtained in this research. In Table II values are given for the total vapour pressures, based on the assumption that the sulphuric acid vapour is always completely dissociated. For solutions containing less than 95% H_2SO_4, the increase in the total vapour pressure due to this factor is very slight. In the last column of Table III are given the values obtained for the boiling points when it is assumed that the sulphuric acid vapour is completely dissociated. These figures approach very closely indeed to the generally accepted values.

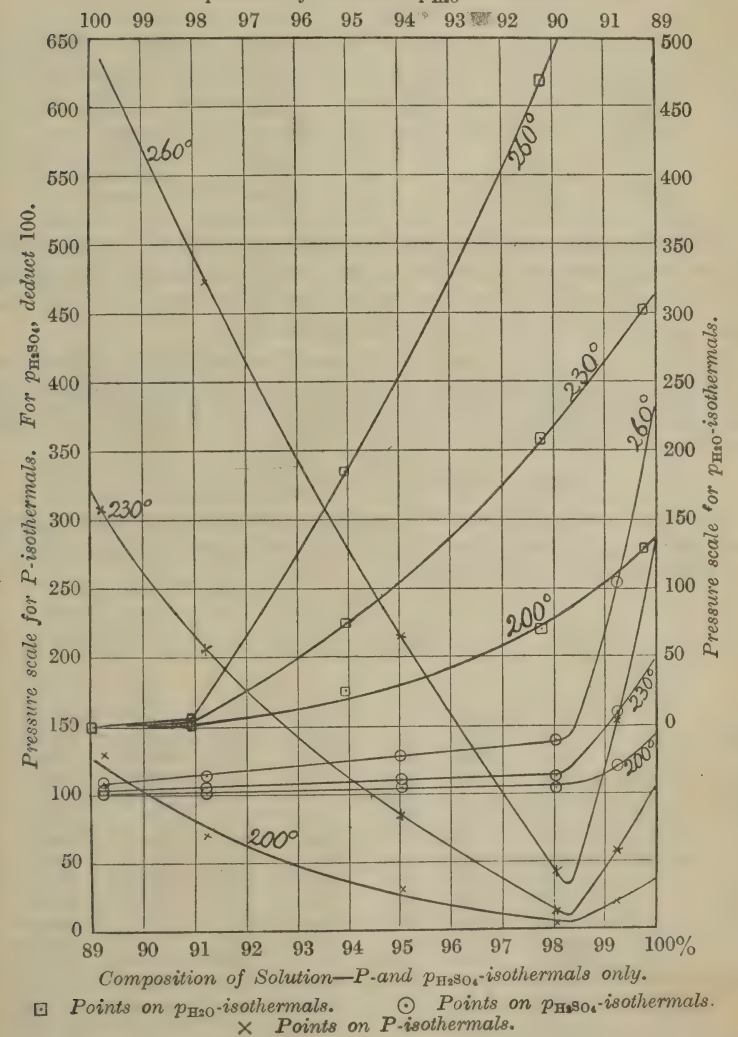
The Variation of the Total Pressure and of the Partial Pressures with the Concentration.

The mode in which the total vapour pressures and the component partial pressures over concentrated sulphuric acid solutions vary when the compositions of these solutions is changed is illustrated in Fig. 2. In this diagram the total pressure, the $p_{H_2SO_4}$- and the p_{H_2O}-isothermals have been drawn for temperatures of 260°, 230°, and 200°. These isothermals are typical.

The form of these curves is striking. In the case of both the $p_{H_2SO_4}$- and the p_{H_2O}-isothermals a sudden and very marked change

of direction occurs when the solution contains 98·2% of sulphuric acid. The total-pressure isothermals exhibit a pronounced minimum at the same composition. This concentration agrees very closely

FIG. 2.



indeed with that of the constant-boiling mixture, which is usually considered to contain 98·3% H_2SO_4.

At this concentration the composition of the liquid and gaseous

phases must be the same and, assuming the vapours in equilibrium with the liquid to behave as perfect gases, the ratio of the two partial pressures should be identical with that of the molecular fractions in the liquid. In Table IV these ratios are compared for a series of temperatures.

TABLE IV.

t.	$p_{H_2SO_4}$.	p_{H_2O}.	$p_{H_2SO_4}/p_{H_2O}$.	$M/(1-M)$.
180°	1·5	0·14	10·7	10·01
200	3·7	0·35	10·5	10·01
220	10·5	0·85	10·23	10·01
240	19·6	1·85	10·05	10·01
260	39·7	3·8	10·45	10·01
280	82·2	8·0	10·27	10·01
300	159·0	15·5	10·30	10·01

When the nature of the partial-pressure curves and the very large variations in pressure which accompany small changes in composition in the neighbourhood of this point are taken into account, the agreement is to be considered quite satisfactory.

Since the partial pressures of both water and sulphuric acid vapour have now been determined, it is possible to test the applicability to concentrated sulphuric acid solutions under the conditions of these experiments of the Duhem—Margules equation

$$d\log p_1/d\log M = d\log p_2/d\log(1-M)$$

in which p_1 and p_2 represent the partial pressures of sulphuric acid and water vapours and M and $1-M$ the molecular fractions of these substances in the liquid mixture.

TABLE V.

t.	Conc. of H_2SO_4. %.	M.	p_1.	p_2.	dp_1.	$-dp_2$.	$-\frac{dp_1}{dp_2}$.	$\frac{p_1}{p_2}\cdot\frac{1-M}{M}$.
180°	89	0·5978	0·30	65	0·09	20·0	0·0045	0·0031
	91	0·6257	0·62	43	0·18	11·0	0·0164	0·0086
	93	0·6864	1·02	26	0·22	9·0	0·0246	0·0179
	95	0·7421	1·55	13	0·27	6·0	0·0458	0·0414
200	89	0·5978	0·86	128	0·25	37·0	0·0067	0·0051
	91	0·6257	1·50	80	0·40	23·5	0·0170	0·0112
	93	0·6864	2·37	44·5	0·48	14·5	0·0331	0·0243
	95	0·7421	3·50	20·5	0·60	10·0	0·0610	0·0593
220	89	0·5978	2·50	240	0·45	57·0	0·0079	0·0069
	91	0·6257	3·65	150·7	0·62	36·0	0·0172	0·0111
	93	0·6864	4·90	89·5	0·85	25·5	0·0383	0·0250
	95	0·7421	6·85	46·0	1·10	18·5	0·0594	0·0517
240	89	0·5978	4·86	406	0·80	90·0	0·0089	0·0081
	91	0·6257	6·9	291	1·05	63·0	0·0167	0·0142
	93	0·6864	9·8	186·5	1·65	40·0	0·0412	0·0240
	95	0·7421	13·3	102·0	2·05	37·0	0·0553	0·0453
260	89	0·5978	8·9	727	2·0	142·0	0·0141	0·0082
	91	0·6257	14·0	502	2·61	100·0	0·0261	0·0167
	93	0·6864	20·1	329	3·39	79·0	0·0429	0·0279
	95	0·7421	27·1	188	3·79	68·5	0·0553	0·0501

The integration of this expression involves certain assumptions regarding the relationship between the partial pressure of each component and the vapour pressure of that component in the pure state. If, however, the equation is written in the form

$$-\frac{dp_1}{dp_2} = \frac{p_1}{p_2} \cdot \frac{1-M}{M}$$

it can be tested by substitution of the values obtained from the isothermals. The estimation of dp_1 and dp_2 was carried out graphically by drawing the approximate tangent to the isothermal at the required point. The results obtained are summarised in Table V.

The values obtained for $p_1/p_2.(1-M)/M$ are invariably lower than those for $-dp_1/dp_2$, but in view of the fact that considerable dissociation of the sulphuric acid vapour probably occurs, close agreement was scarcely to be expected.

Summary.

1. The partial pressures of the water vapour in contact with acid–water mixtures containing from 89% to 99·3% of sulphuric acid have been determined at temperatures ranging from 180° to 300° by a method previously described.

2. The previously determined values of the sulphuric acid partial pressures were vitiated by adsorption of acid vapour on the glass wool employed to prevent mechanical transference of liquid, and have been redetermined.

3. Both the water and the sulphuric acid partial pressures, and also the total pressure, can be represented by Rankine's equation

$$\log p = \alpha - \beta/T - \gamma \log T,$$

for which the various constants have been calculated.

4. The boiling points obtained from the total pressure by extrapolation are considerably too high. If, however, it is assumed that complete dissociation of the sulphuric acid vapour occurs, values are obtained which are in good agreement with the accepted values.

5. The $p_{H_2SO_4}$-, p_{H_2O}-, and P-isothermals have been constructed for temperatures of 260°, 230°, and 200°. The P-isothermals exhibit a sharp minimum at a composition 98·2% H_2SO_4. The form of the partial pressure curves is in qualitative agreement with the Duhem–Margules equation. The quantitative agreement, however, is not close, probably on account of dissociation of the acid vapour.

The University, Cape Town. [*Received, March 16th*, 1925.]

CCCXCI.—*The Partial Formaldehyde Vapour Pressures of Aqueous Solutions of Formaldehyde. Part II.*

By Wilfrid Ledbury and Ethelbert William Blair.

The investigation of the partial formaldehyde vapour pressures of aqueous formaldehyde solutions, described in Part I (this vol., p. 26), showed that, following a prolonged initial exposure at 15°, equilibrium between the liquid and vapour phases was only gradually attained when the temperature of a solution was subsequently changed to 20° or 0°. An explanation of this was based upon the assumption that a new equilibrium between complex (polymerised, hydrated, etc.) and simple molecules in solution, depending on the temperature, was gradually approached as time elapsed. The presence in aqueous formaldehyde solution of both the polymerised and monomolecular forms is made evident by the work of Auerbach and Barschall (*Arb. Kais. Ges.-A.*, 1905, **22**, 584; *Chem. Centr.*, 1905, II, 1081), who carried out molecular-weight determinations by the cryoscopic method. These determinations indicated that in solutions containing 37—38% (by vol.) of formaldehyde, there probably exist polymerides of complexity greater than trimolecular. Auerbach and Barschall concluded that the equilibrium between the different molecular forms of formaldehyde is reversible, so that the condition of aqueous solutions of formaldehyde, a short time after preparation, depends only on the concentration and temperature. In order to study further the influence of temperature and solution concentration on the partial formaldehyde vapour pressures of aqueous formaldehyde solutions, determinations have been carried out at 35° and 45°, and these new data correlated with those previously obtained at 0° and 20°.

It has been previously pointed out by the authors that methyl alcohol, when present in small amounts (compare the proportion of methyl alcohol to formaldehyde in commercial formalin), considerably enhances the partial formaldehyde vapour pressures of formaldehyde solutions at 20°. Formaldehyde in methyl-alcoholic solution and in a mixture of water and methyl alcohol, containing a large proportion of the latter, has since been investigated in this connexion, and also the effect of the presence of small amounts of the alcohol in formaldehyde solutions at 35° and 45°.

Experimental.

Method and Apparatus.—Aqueous solutions of formaldehyde, free from methyl alcohol, were prepared either by the method of continuous refluxing previously described or by dissolving solid para-

formaldehyde, uncontaminated with methyl alcohol, in boiling water. The solutions so prepared were kept for 2 or 3 weeks at room temperature; it was then assumed that the equilibrium between the different molecular species of formaldehyde in solution had attained a value dependent only on the concentration and temperature of exposure, irrespective of the method of preparation (Auerbach and Barschall, *loc. cit.*; Auerbach and Plüddemann, *ibid.*, 1914, **47**, 116). To ascertain the effect of the presence of small amounts of methyl alcohol on the partial formaldehyde vapour pressures of the solutions, the alcohol, having an acetone content of less than 0·10%, was added to a series of the solutions in such amounts as to provide a constant ratio, CH_4O/CH_2O. For the preparation of formaldehyde in methyl-alcoholic solution, a current of dry nitrogen was passed over paraformaldehyde in a silica tube at 170°. Formaldehyde vapour, carried forward by the gas-stream, was absorbed in methyl alcohol, as free as possible from acetone. The solution was filtered from any insoluble polyoxymethylenes and kept several weeks before use. This solution has an exceptionally irritant action on the membranes of the eyes and nose. Unlike aqueous formaldehyde, it produces this effect after a minute or so.

The formaldehyde content (*ca.* 15%) of this solution was estimated both before and after refluxing with dilute sulphuric acid, and the difference in the values showed that the equivalent of about 5 g. of formaldehyde per 100 c.c. was combined as methylal. When a methyl-alcoholic solution of formaldehyde was prepared by heating an excess of pure paraformaldehyde with methyl alcohol in a sealed tube for 6 hours at 120°, the major portion of the aldehyde in solution was combined as methylal. The free formaldehyde content was 6·63 g. per 100 c.c., whilst the methylal present was equivalent to 12·0 g. per 100 c.c. Refluxing paraformaldehyde with methyl alcohol at the ordinary pressure for 2 days yielded a solution containing 5·16 g. of free formaldehyde and 1·44 g. of combined formaldehyde per 100 c.c.

As in the corresponding determinations at 20° and 0°, the "dynamic" or "flow" method was employed for the series of experiments at 35° and 45°. The apparatus used was similar to that described in Part I, except that a heating unit of 500 watts was substituted for the small carbon-filament lamp. Since accurate estimations of small amounts of formaldehyde are possible by the use of the iodometric method of Romijn (*Analyst*, 1897, **22**, 221; see also *Chem.-Ztg.*, 1901, **25**, 74; *Ber.*, 1898, **31**, 1979; 1901, **34**, 2817), it was necessary to pass volumes of air of only 2 or 3 litres at the most for each vapour pressure determination. During the course of a run, involving several successive determinations on the

same solution, the alteration of the strength of the formaldehyde solution in the "carburettors" was thus made negligible, even in the case of concentrated solutions at 45° (compare Part I). De Waal (*Pharm. Weekblad*, 1907, **44**, 1207; *J. Pharm. Chim.*, 1907, **26**, 498) has shown that in presence of air increase of temperature promotes oxidation of formaldehyde in solution, but that this is slight even at 50°, after an exposure for 400 hours. In the present series of determinations, air was passed at the rate of about 1 litre in 3 hours. All estimations of formaldehyde and methyl alcohol were carried out as previously described, and a similar procedure of experimentation was followed.

Formaldehyde Vapour Pressures of Aqueous Formaldehyde Solutions at 35° and 45°.

For solutions of formaldehyde not containing methyl alcohol, the vapour pressure values at 35°, obtained after the passage of several litres of air (for successive determinations), were slightly higher than those obtained at the outset. This increase, however, was not nearly so marked as at 20°, and the eventual steady maximum was more rapidly reached. Solutions containing methyl alcohol each gave a series of practically identical values from the beginning, and this was also the case with both sets of solutions at 45°. It is evident that, at the temperatures under consideration, the new equilibrium between the various molecular species in solution is attained much more rapidly than at 0° or 20°. The equilibrium values of the formaldehyde vapour pressures for formaldehyde solutions free from methyl alcohol, at 35°, are in Table I, and the corresponding values for solutions containing methyl alcohol ($CH_4O/CH_2O = 0{\cdot}13$) in Table II. (In Tables I—V, g = grams of formaldehyde in 100 c.c. of formalin solution, m_t = mg. of formaldehyde vapour in 1 litre of issuing air at $t°$, and p = partial pressure of formaldehyde vapour in mm. of Hg.). Curves A and B in Fig. 1 represent the relationship between concentration of solution and partial pressure at 35° for pure solutions and for solutions containing methyl alcohol, respectively.

TABLE I.

g	1·09	5·15	11·8	18·6	20·8	31·0	39·5
$m_{35°}$	0·27	1·13	2·06	2·87	3·17	4·27	4·58
p	0·166	0·695	1·29	1·80	1·94	2·48	2·81

TABLE II.

g ($CH_4O/CH_2O = 0{\cdot}13$)	5·24	13·05	23·7	38·3
$m_{35°}$	1·200	2·52	3·97	5·39
p	0·735	1·56	2·45	3·34

The data obtained from solutions at 45° are in Tables III and IV, and the curves showing variation of formaldehyde vapour pressure with solution concentration are plotted in Fig. 2.

TABLE III.

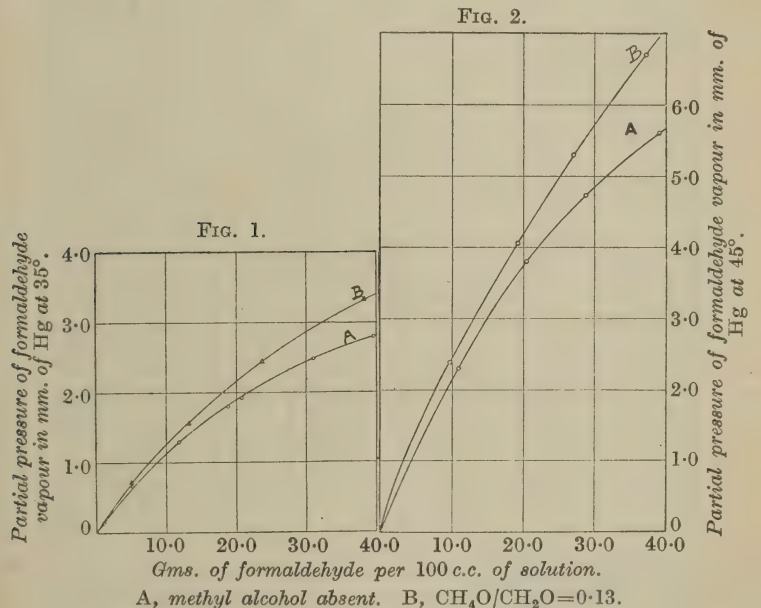
g	10·8	20·4	28·75	39·2
$m_{45°}$	3·77	6·17	7·70	9·12
p	2·30	3·79	4·72	5·60

TABLE IV.

g ($CH_4O/CH_2O = 0·13$)	9·76	19·15	27·0	37·1
$m_{45°}$	3·88	6·62	8·62	10·9
p	2·39	4·07	5·3	6·68

FIG. 1.

FIG. 2.

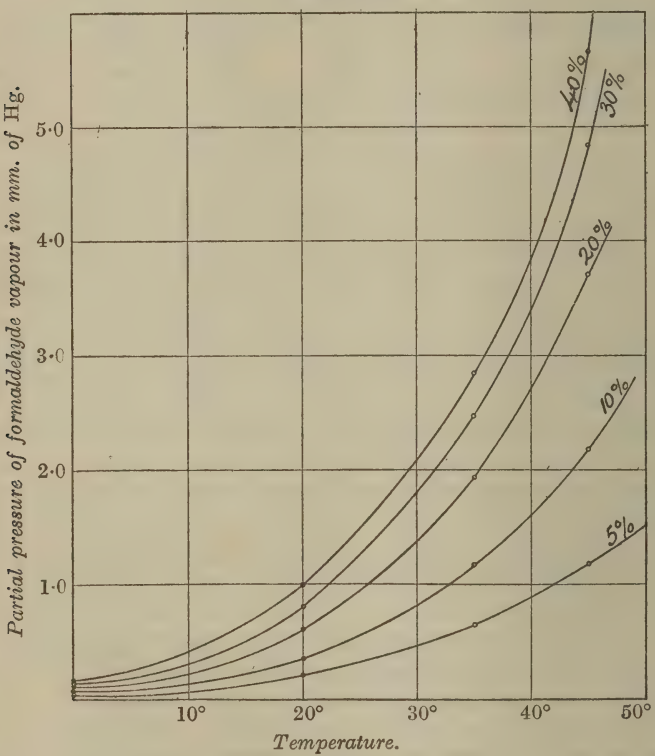


Variation with Temperature of the Partial Formaldehyde Vapour Pressures of Aqueous Formaldehyde Solutions.

From data derived from the curves, drawn to represent the variation of partial formaldehyde vapour pressure with solution concentration at particular temperatures, *viz.*, 0°, 20°, 35°, and 45°, the graphs of Fig. 3 have been plotted to illustrate the manner in which the partial pressures change with temperature. The latter curves are plotted for solutions containing, respectively, 5, 10, 20, 30, and 40 g. of formaldehyde in 100 c.c. It is apparent that the differences between the partial pressures of the more concentrated

solutions at a given temperature are less marked than in the case of the weaker solutions. The data from molecular-weight determinations, the low values of the partial formaldehyde vapour pressures at the temperatures under consideration, and the gradually diminishing dp/dg of the vapour pressure–concentration curves demonstrate the increasing preponderance of polymerides in formalin solutions with increasing concentration. The relatively high

FIG. 3.



concentrations of polymerised formaldehyde in the stronger solutions explains the particular characteristic of the curves referred to above.

When the logarithms of the partial formaldehyde vapour pressures ($\log p$) are plotted against the reciprocals of the absolute temperature ($1/T$) for solutions of given strengths, a series of almost parallel straight lines is obtained. In Fig. 4, the curves indicate the straight-line relationships between $\log_{10} p$ and $1/T$ for solutions having formaldehyde contents of 10, 20, 30, and 40 g. per 100 c.c.,

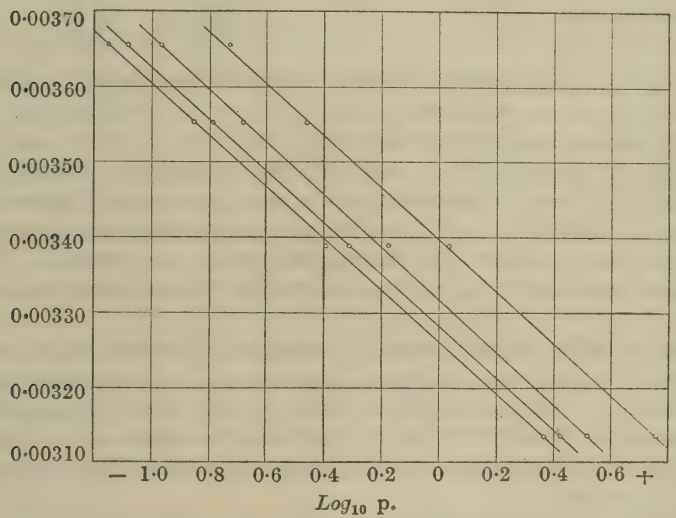
respectively. Thus the formaldehyde partial vapour pressure of any aqueous formaldehyde solution up to a 40% concentration can be expressed, for the temperatures under consideration, by a simplified form of Rankine's equation (*Edinburgh New Phil. J.*, July, 1849) connecting vapour pressure and temperature :

$$\log_{10} p = \alpha - B/T,$$

where $\alpha_{10\%} = 9{\cdot}47$, $\alpha_{20\%} = 9{\cdot}70$, $\alpha_{30\%} = 9{\cdot}81$, $\alpha_{40\%} = 9{\cdot}87$, (approx.) and β (for all solutions up to 40%) = 2905 (approx.).

A straight-line relationship is somewhat deviated from when $\log_{10} p$ for any given solution strength is plotted against T. The formula $\log p = \alpha + \beta T + \gamma T^2 + \ldots$., which Perman (J., 1903,

FIG. 4.



88, 1168) successfully applied to aqueous solutions of ammonia, was found to be inapplicable to aqueous solutions of formaldehyde.

Methyl-alcoholic Solution of Formaldehyde.—Prior to the determination of the partial formaldehyde vapour pressure at 20° of a methyl-alcoholic solution (15·9 g. CH_2O per 100 c.c.), blank determinations were carried out on a sample of the methyl alcohol employed, since, although this alcohol was the purest obtainable, it was not quite free from acetone (less than 0·10%). At 20°, the blank values were equivalent to about 0·1 mm. of formaldehyde, estimations being carried out iodometrically. Further vapour-pressure determinations have been carried out at 20° and 0° on formaldehyde in methyl alcohol–water solution, the alcohol being present in preponderating amount. This latter solution was obtained by

diluting with water the original 15% methyl-alcoholic solution in order to obtain a liquor containing 10 g. of free formaldehyde per 100 c.c. Blanks were performed at 20° and 0° on a mixture of methyl alcohol and water, in which the proportions of the two components were the same as in the formaldehyde solution examined. The data obtained are in Table V: solution *A* contained 15·97 g. of free formaldehyde (equivalent of 5·0% formaldehyde as methylal) in 100 c.c. of methyl-alcoholic solution; solution *B* contained 10 g. of free formaldehyde, 59 g. of methyl alcohol, and 26·7 g. of water in 100 c.c.

TABLE V.

Solution.	*t*.	m_f.	*p*.
A	20°	3·68	2·27
B	20	1·93	1·16
B	0	0·390	0·234

It will be seen that at 20° the partial formaldehyde vapour pressure of an approximately 15% solution of formaldehyde in methyl alcohol is almost *five* times the value of that for an aqueous solution of corresponding strength. For a solution containing about 60% of methyl alcohol there is an approximately threefold increase at both 20° and 0° over an aqueous solution containing a corresponding amount of formaldehyde (10 g. per 100 c.c.). In all cases, practically constant vapour pressure values were obtained from the outset.

Since methylal vapour, carried forward from the methyl-alcoholic solution to the absorption worms, does not affect the iodometric estimation of the formaldehyde fixed by the water (Bergstrom, *J. Amer. Chem. Soc.*, 1923, **45**, 2150), the figure obtained represents the partial vapour pressure of uncombined formaldehyde in methyl-alcoholic solution.

If it be assumed that the methylal (which is present to the extent of the equivalent of 5 g. of formaldehyde per 100 c.c. of 15% methyl-alcoholic solution) does not exert a *very* pronounced influence, in its solvent capacity, on the partial vapour pressure of the free formaldehyde in solution, then it is found that the application of the simple mixture rule to a 15% aqueous solution, in which $CH_4O/CH_2O = 0{\cdot}13$, by no means accounts for the enhanced value at 20° brought about by the addition of the alcohol to the original aqueous formalin, *i.e.*, from 0·49 to 0·59 mm. Hg.

It has been pointed out that the removal of methyl alcohol from commercial formalin (40% by vol.) increases the tendency of paraformaldehyde to separate from solution. Experiments have shown, however, that paraformaldehyde is more readily soluble in water than in methyl alcohol; thus the precipitation of paraformaldehyde

from formalin, which has been freed from methyl alcohol, cannot be attributed to the removal of a constituent having a greater solvent capacity for formaldehyde. It therefore appears that the presence of methyl alcohol in aqueous formaldehyde solutions must bring about an alteration of the equilibrium between simple and complex molecules in such a way as to enhance considerably the concentration of mono-molecular formaldehyde. The consequent decrease in the concentration of the polymerides naturally decreases their liability to precipitation as paraformaldehyde. Such an effect on the above-mentioned equilibrium serves to explain why methyl alcohol, present in small amount in an aqueous formaldehyde solution, increases the partial formaldehyde vapour pressure to an extent beyond that anticipated from the application of the simple mixture rule. It is here assumed, as hitherto, that the formaldehyde vapour pressure is almost entirely dependent on the concentration of the simple molecular form of the aldehyde.

Summary.

The partial formaldehyde vapour pressures of aqueous solutions of formaldehyde, free from methyl alcohol, have been determined by the dynamic method at 35° and 45°. Corresponding determinations, carried out on solutions of formaldehyde containing small amounts of methyl alcohol ($CH_4O/CH_2O = 0{\cdot}13$), have shown that the influence of the alcohol in enhancing the vapour pressures is similar to that noted at 20°. The effect of increased temperature in bringing about a more rapid adjustment of equilibrium conditions has also been shown.

From the vapour pressure values a relationship connecting functions of the vapour pressure and the temperature has been derived.

The partial formaldehyde vapour pressure of a methyl-alcoholic solution of formaldehyde has been determined, and the influence of methyl alcohol on the formaldehyde vapour pressures of aqueous formaldehyde solutions considered.

The authors desire to express their thanks to the Department of Scientific and Industrial Research and to the Admiralty for permission to publish these results.

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CCCXCII.—*Transformations of the Sugar Nitrates.*

By JOHN WALTER HYDE OLDHAM.

ALTHOUGH the nitrates of the sugar group are, as a rule, definitely crystalline and easily adaptable to synthetical operations, little use seems to have been made of them since they were studied by Will and Lenze (*Ber.*, 1898, **31**, 68) and Koenigs and Knorr (*Ber.*, 1901, **34**, 957).

When 2 : 3 : 5-trimethyl glucosan, dissolved in chloroform, is acted on by fuming nitric acid under the conditions described in the experimental part, *trimethyl glucose dinitrate* is obtained. The result is striking, particularly as the action of the same reagent on 1 : 6-diacetyl 2 : 3 : 5-trimethyl glucose yielded a syrup which failed to crystallise. Trimethyl glucose dinitrate has no action on Fehling's solution, either before or after acid hydrolysis. The nitrate group in position 1 can be replaced by methoxyl by boiling with methyl alcohol in presence of barium carbonate, the reaction yielding *trimethyl methylglucoside* 6-*mononitrate*. This mononitrate is converted on hydrolysis into the same trimethyl methylglucoside as is obtained from trimethyl glucosan, and the nitrate group was definitely allocated to the 6 position by the fact that, on treatment with sodium iodide, the same trimethyl methylglucoside iodohydrin was readily produced as that already obtained from Fischer's acetodibromoglucose (Irvine and Oldham, this vol., p. 2729). This sequence of changes indicates that the nitrate group possesses considerable reactivity, yet the compound was recovered unchanged (as was also methylglucoside 6-mononitrate) when heated with alcoholic ammonia, as described by Wallach (*Ber.*, 1881, **14**, 422).

In the parallel case of triacetyl glucosan, the action of fuming nitric acid was more complex and a yellow syrup showing a high nitrogen content was invariably produced, together with *triacetyl glucose* 1 : 6-*dinitrate*, which was isolated in fair yield. The compound had likewise no action on Fehling's solution before or after acid hydrolysis, but was readily converted into derivatives of different types. On boiling in glacial acetic acid solution with sodium acetate, it was converted into *tetra-acetyl glucose* 6-*mononitrate;* and this on hydrolysis yielded a *tetra-acetyl glucose*, isomeric with that already obtained by Fischer, in that the sixth hydroxyl group in place of the first is unsubstituted. Further, although triacetyl glucose dinitrate reacted with methyl alcohol only with great difficulty, yields of 50—60% of the corresponding *triacetyl methylglucoside* 6-*mononitrate* were obtained. This compound was converted into *triacetyl methylglucoside* on hydrolysis and into

triacetyl methylglucoside 6-*iodohydrin* on treatment with sodium iodide in acetone in the manner described by Irvine and Oldham (*loc. cit.*).

Methylglucoside 6-*mononitrate* obtained by the action of ammonia on the corresponding acetyl derivative could not be isolated, as it could not be separated from acetamide. By the action of dimethylamine and removal of the acetodimethylamide, however, the mononitrate of the parent glucoside was isolated as a syrup which failed to crystallise. By means of the silver oxide reaction, this compound was converted into the trimethyl methylglucoside 6-mononitrate already described, thus establishing the constitution of the complete series of new derivatives. Triacetyl methylglucoside 6-iodohydrin, on treatment with dimethylamine in the manner already described, gave a somewhat poor yield of *methylglucoside* 6-*iodohydrin*. Finally, incidental evidence was obtained, in the course of large-scale preparations of triacetyl methylglucoside 6-mononitrate, that degradation to the pentose series had taken place to a limited extent.

Synthetical and constitutional studies based on the method of nitrate formation now communicated are in progress.

Experimental.

2 : 3 : 5-*Trimethyl Glucose* 1 : 6-*Dinitrate*.—A solution of trimethyl glucosan (5 g.) in a mixture of 60 c.c. of fuming nitric acid and 40 c.c. of chloroform containing a few grams of phosphorus pentoxide was kept for 19 hours at the ordinary temperature. The specific rotation increased from $-64°$ to $+140·7°$, calculated on the change in concentration due to the addition of two nitrate groups. The mixture was poured slowly with constant stirring into ice, the lower layer separated, washed once with ice-cold water, and taken to dryness below 60° in a vacuum. The *dinitrate* crystallised from absolute alcohol in colourless needles, m. p. 86° (Found : OMe, 30·3; N, 9·1. $C_9H_{16}O_{10}N_2$ requires OMe, 29·8; N, 9·0). The compound is sparingly soluble in alcohol, insoluble in water or light petroleum, and soluble in other solvents. $[\alpha]_D + 149·3°$ in chloroform (*c*, 2·3193), $+151·7°$ in acetone (*c*, 1·463), $+144·8°$ in methyl alcohol (*c*, 1·508), and $+147·2°$ in a mixture of 60% of fuming nitric acid and 40% of chloroform by volume (*c*, 2·915).

Trimethyl Methylglucoside 6-*Mononitrate*.—The dinitrate was boiled in 5% solution in methyl alcohol for ½ hour in presence of barium carbonate. The product, isolated in the usual manner (yield 90%), was drained on a tile and recrystallised from light petroleum; it then melted at 53—54°, n_D of the superfused substance = 1·4565 (Found : C, 42·7; H, 6·7; OMe, 44·1; N, 4·95. $C_{10}H_{19}O_8N$ requires C, 42·7; H, 6·8; OMe, 44·1; N, 5·0%). The

mononitrate is insoluble in water, but soluble in all other solvents. $[\alpha]_D$ — 5·2° in chloroform (*c*, 2·0653), — 4·4° in acetone (*c*, 3·5845), and — 1·3° in methyl alcohol (*c*, 3·3413).

Conversion of Trimethyl Methylglucoside 6-Mononitrate into Trimethyl Methylglucoside.—The compound was hydrolysed by boiling with iron dust in glacial acetic acid, in not more than 5% concentration, until a few drops of the liquid gave no trace of blue colour on standing for some time with a strong solution of diphenylamine in concentrated sulphuric acid. (This reaction is given by all these compounds, and constitutes an extremely delicate test for the presence of a nitrate group.) The solution was then filtered, the residue washed with glacial acetic acid, and the filtrate poured into water containing a fair quantity of dissolved sodium acetate, the object of which was to suppress the hydrogen chloride set free by the chloroform with which the solution was repeatedly extracted. The trimethyl methylglucoside thus removed, on recrystallisation from light petroleum, showed the correct melting point and mixed melting point. The yield was good.

Conversion into the Corresponding Iodohydrin.—On treating the mononitrate with sodium iodide in the manner already described (Irvine and Oldham, this vol., p. 2729), a good yield of crystals was obtained, m. p. 31—33°, which showed no depression on mixing with a sample of the authentic iodohydrin.

Preparation of Triacetyl Glucose 1 : 6-Dinitrate.—The best conditions as yet found are the following : Triacetyl glucosan (5 g.) was dissolved in a mixture of 30% of chloroform with 70% of redistilled nitric acid * by volume, solid nitrogen pentoxide (10 g.) added, and the whole made up to 100 c.c. with chloroform and kept at the ordinary temperature for about 110 hours. The specific rotation of the solution was then about + 138°. Sometimes the liquid separates into two layers; should these not disappear towards the end of the reaction, the system can be made homogeneous by the addition of a small measured amount of fuming nitric acid. The product was isolated in the manner described for the corresponding methylated derivative and washed with cold absolute alcohol (yield about 65%). On recrystallisation from hot absolute alcohol, this yield was diminished by nearly half and the product melted at 132—133°. The substance is insoluble in water, light petroleum, or cold ethyl alcohol, sparingly soluble in ether or cold methyl alcohol,

* In this paper, the expression " fuming nitric acid " refers to the product obtained by distilling ordinary concentrated nitric acid over its own volume of concentrated sulphuric acid. " Redistilled nitric acid " refers to a product, *d* 1·54, obtained by distilling " fuming nitric acid " over twice its volume of concentrated sulphuric acid.

and soluble in other solvents. The rotation of the pure compound in a mixture of fuming nitric acid and chloroform similar to that used in the preparation was $[\alpha]_D + 144{\cdot}2°$ for $c = 5{\cdot}0$. The substance has not been analysed, as it is difficult to obtain a perfectly pure specimen, but in view of the derivatives into which it can be transformed there can be little doubt that it consists of *triacetyl glucose* 1 : 6-*dinitrate*.

Tetra-acetyl Glucose 6-*Mononitrate*.—The dinitrate was boiled for 1—1½ hours with a mixture of acetic acid, acetic anhydride, and sodium acetate. If the dinitrate was pure, scarcely any colour was developed; but if not, the solution coloured deeply. In the former case, the reaction was practically quantitative, as was shown by the specific rotation falling from + 144° to + 23·3°, the corresponding value of the pure substance in acetic acid being + 23·2°. The product was poured into water, when about 80% of it separated almost immediately in a crystalline condition; the remainder, however, sometimes took several days to separate. The product after recrystallisation from absolute alcohol melted at 142—143°, reduced Fehling's solution strongly on boiling, was insoluble in water or light petroleum, sparingly soluble in ether or alcohol, and soluble in other solvents (Found : C, 42·55; H, 5·0; N, 3·65. $C_{14}H_{19}O_{12}N$ requires C, 42·7; H, 4·8; N, 3·6%). $[\alpha]_D + 23{\cdot}2°$ in glacial acetic acid (*c*, 2·494) and + 27·2° in chloroform (*c*, 2·038).

Tetra-acetyl Glucose.—The 6-mononitrate was hydrolysed with iron dust in glacial acetic acid exactly as described in the case of the corresponding methylated compound. *Tetra-acetyl glucose* crystallised from ether in colourless needles, m. p. 126·5—127·5°, $[\alpha]_D + 9{\cdot}8°$ in chloroform (*c*, 0·816) (Found : $C_2H_4O_2$, after allowance for the alkali used by the reducing sugar, 68·7. Calc., $C_2H_4O_2$, 68·9%). The substance is insoluble in cold water or light petroleum, sparingly soluble in ether, soluble in hot water and in organic solvents generally.

The above reaction is rather uncertain, as sometimes the product failed to crystallise.

Triacetyl Methylglucoside 6-*Mononitrate*.—Triacetyl glucose dinitrate, unlike both acetonitroglucose and the corresponding methylated derivative, reacted only with great difficulty with methyl alcohol in presence of barium carbonate, even when a small quantity of pyridine was added as recommended by Koenigs and Knorr (*loc. cit.*). On boiling the mixture for 24 hours, the specific rotation of the solution became constant at + 5·0°. The solution was filtered, and the solid well washed with chloroform. The washings were used to dissolve the residue left on evaporation of the methyl-alcoholic filtrate, in order to purify it from traces of barium nitrate. After removal of the chloroform, the red residue, crystallised twice

from absolute alcohol, melted at 133·5—134·5° (yield 50—60%), and was insoluble in water or light petroleum, sparingly soluble in ether or cold ethyl or methyl alcohol, and soluble in other solvents (Found : C, 42·8; H, 5·35; N, 3·8; OMe, 8·6; $CH_3{\cdot}CO_2H$, 66·0. $C_{13}H_{19}O_{11}N$ requires C, 42·7; H, 5·2; N, 3·8; OMe, 8·5; $CH_3{\cdot}CO_2H$, 65·7%). $[\alpha]_D$ — 14·3° in chloroform (*c*, 5·964) and — 14·1° in acetone (*c*, 2·6913). If the substance is boiled with methyl-alcoholic sodium methoxide, the specific rotation falls to — 115°, allowance being made for the change in concentration due to loss of acyl groups, which corresponds to the formation of about 80% of Fischer's anhydro-methylglucoside.

Triacetyl Methylglucoside.—On hydrolysing the nitrate with iron dust in glacial acetic acid in the manner already described, *triacetyl methylglucoside* was obtained, in good yield, in colourless crystals, melting after recrystallisation from ether at 134—134·5°; $[\alpha]_D$ in chloroform = — 19·1° for *c* = 1·514 (Found : OMe, 9·5; $CH_3{\cdot}CO_2H$, 54·6. $C_{13}H_{20}O_9$ requires OMe, 9·6; $CH_3{\cdot}CO_2H$, 56·2%). The compound is insoluble in cold water or light petroleum, but soluble in other solvents including hot water.

Methylglucoside 6-*Mononitrate.*—Triacetyl methylglucoside 6-mononitrate was treated with a 5% methyl-alcoholic solution of dimethylamine, and the acetodimethylamide produced was distilled off in a vacuum at 100°; the residual syrup failed to crystallise (Found : N, 5·9; HNO_3, 25·7. $C_7H_{13}O_8N$ requires N, 5·85; HNO_3, 26·3%). A specimen of the substance was twice methylated by the silver oxide reaction; the product crystallised on nucleation with trimethyl methylglucoside 6-mononitrate obtained as described above. After draining on a tile and recrystallisation from light petroleum, the compound showed the correct melting point and mixed melting point, thus proving the constitution of this series of substances.

Triacetyl Methylglucoside 6-*Iodohydrin.*—For the sake of comparison, triacetyl methylglucoside 6-mononitrate was treated with sodium iodide in acetone in the manner already described. The product, after recrystallisation from aqueous alcohol, consisted of colourless needles, m. p. 111—112·5°, which were insoluble in water or light petroleum but soluble in other solvents. The yield was poor [Found : OMe, 7·4; I, 28·0; $CH_3{\cdot}CO_2H$ (I being calculated as $CH_3{\cdot}CO_2H$), 56·4. $C_{13}H_{19}O_8I$ requires OMe, 7·2; I, 29·5; $CH_3{\cdot}CO_2H$, 55·8%). The specific rotation in chloroform was + 0·9° for *c* = 3·027.

Methylglucoside 6-*Iodohydrin.*—On treatment with dimethylamine in the manner already described, the preceding triacetyl derivative was converted into the parent glucoside in bad yield. The product, which consisted when pure of colourless crystals, but

was usually slightly pink, melted at 157—158°, was insoluble in ether or light petroleum, very sparingly soluble in chloroform, slightly more soluble in acetone, and soluble in other solvents. The best recrystallising medium was a mixture of chloroform and ethyl acetate (Found: OMe, 10·3; I, 41·7. $C_7H_{13}O_5I$ requires OMe, 10·1; I, 41·7%). $[\alpha]_D$ in chloroform = − 16·1° for c = 1·677.

Acetonitropentose.—On taking to dryness the mother-liquors from the recrystallisation of triacetyl methylglucoside 6-mononitrate, boiling for ½ hour with acetic anhydride and sodium acetate, and pouring into water, a precipitate was obtained which, after very many recrystallisations from absolute alcohol, melted at 168—169°. The compound did not reduce Fehling's solution, and was at first thought to be the α-form of triacetyl methylglucoside 6-mononitrate. It contained no methoxyl, however, and the analytical figures are in close agreement with those required for a triacetyl pentose mononitrate (Found: C, 41·2; H, 4·7; N, 4·2. $C_{11}H_{15}O_{10}N$ requires C, 41·1; H, 4·7; N, 4·4%). The substance had the same solubilities as triacetyl glucose dinitrate, and showed specific rotation in chloroform = + 92·0° for c = 1·214.

The author wishes to express his indebtedness to the Carnegie Trust, and also to Principal Sir James C. Irvine for much valuable advice and for the kindly interest he has always shown in the work.

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UNIVERSITY OF ST. ANDREWS. [*Received, October 26th,* 1925.]

CCCXCIII.—*Lead Dihydride and Lead Tetrahydride.*

By EDWARD JOSEPH WEEKS.

SOLID hydrides of arsenic (*Chem. News*, 1924, **129**, 31), antimony (this vol., p. 1069), and bismuth (*ibid.*, p. 1799) having been prepared, the existence of a solid lead hydride was investigated. To a solution of alkali plumbite made from lead acetate and caustic soda or potash, pure aluminium foil was added. The grey deposit obtained was washed many times with caustic potash solution and finally with water until the washings were neutral. It was filtered off, and dried in a vacuum desiccator over sulphuric acid for 3—5 days, both operations being performed in an atmosphere of hydrogen. The action follows the equation $2KHPbO_2 + 2Al = 2KAlO_2 + Pb_2H_2$. The deposit contained lead and hydrogen only, and on heating in a vacuum gave off hydrogen and left metallic lead. Details of the method of analysis have already been given for bismuth (*loc. cit.*). 0·3253 G. gave 20 c.c. of H_2 measured at *N.T.P.* and 0·3243 g. of

Pb. H, 0·5; Pb, 99·1%. 0·1504 G. gave 10 c.c. of H_2 at *N.T.P.* and 0·1422 g. of Pb. H, 0·6; Pb, 99·5%. On combustion, 1·9550 g. gave 0·0662 g. of H_2O. H, 0·5% (Pb_2H_2 requires Pb, 99·5; H, 0·5%).

Lead dihydride heated in a tube in the absence of air gave lead and hydrogen only. No trace of PbH_4 appeared to be formed, as no lead deposit could be obtained on heating the issuing gas. The dihydride oxidises rapidly in the air and therefore must be kept in an inert gas. Fused potassium nitrate reacted vigorously with it (as with As_2H_2; Sb_2H_2; Bi_2H_2), but only slowly oxidised finely divided lead.

To obtain the tetrahydride, first prepared by Paneth, the dihydride was heated in a silica tube in an atmosphere of pure hydrogen, and the issuing gas was passed through a heated tube; a deposit of lead was then obtained. With hydrogen alone, no deposit was formed and hence it is concluded that the reduction of Pb_2H_2 follows the equation $Pb_2H_2 + 3H_2 = 2PbH_4$.

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CCCXCIV.—*Complex Formation in Lead Nitrate Solutions. Part II. The Quaternary System Potassium Nitrate–Lead Nitrate–Barium Nitrate–Water.*

By SAMUEL GLASSTONE and ERNEST J. RIGGS.

THE primary object of the present work was to investigate the quaternary system lead nitrate–barium nitrate–potassium nitrate–water at 25° and at 50°, and hence it was required to have a knowledge of the three ternary systems KNO_3–$Pb(NO_3)_2$–H_2O, KNO_3–$Ba(NO_3)_2$–H_2O and $Pb(NO_3)_2$–$Ba(NO_3)_2$–H_2O, at the same temperatures. The first of these three systems has been investigated by Glasstone and Saunders (J., 1923, **123**, 2134) at 25° and 50°; the second has been examined at 9·1°, 21·1° and 35° by Findlay, Morgan, and Morris (*ibid.*, 1914, **105**, 779) and to a limited extent at 25° by Foote (*Amer. Chem. J.*, 1904, **32**, 251); the 25°-isothermal for the third system was investigated by Fock (*Z. Kryst.*, 1897, **28**, 337). Before the quaternary system was examined, therefore, Foote's measurements on the ternary system KNO_3–$Ba(NO_3)_2$–H_2O at 25° were extended and the 50°-isotherm was determined completely; Fock's work at 25° was repeated because this author did not use the Schreinemakers residue method for the determination of the composition of the solid phase, and the 50°-isotherm for the system

$Pb(NO_3)_2$–$Ba(NO_3)_2$–H_2O was also determined. Finally, the quaternary system $Pb(NO_3)_2$–$Ba(NO_3)_2$–KNO_3–H_2O was investigated as completely as possible at 25° and 50°. It was hoped to obtain through this investigation further evidence for the existence of a double or complex salt of lead nitrate and potassium nitrate, the presence of which has already been suspected in solutions containing these two salts (see Glasstone and Saunders, *loc. cit.*). Lead and barium nitrates have an almost identical crystal structure (Vegard, *Z. Physik*, 1922, **9**, 395) and separate from solutions containing both salts as a continuous series of mixed crystals; further, potassium and barium nitrates form a double salt, $2KNO_3,Ba(NO_3)_2$ (Foote, *loc. cit.*), and consequently it was thought possible that when this double salt separated from a solution containing lead, barium, and potassium nitrates there might be a tendency for a potassium nitrate–lead nitrate double salt with a similar structure, which has no stable existence at the ordinary temperature, to separate with it as a mixed crystal. This idea was based on the well-known existence of $CuSO_4,7H_2O$ in the form of a mixed crystal with $FeSO_4,7H_2O$, and the recent preparation by Richards and Meldrum (*J. Amer. Chem. Soc.*, 1921, **43**, 1543) of $Na_2SO_4,4H_2O$, which does not exist by itself, as a mixed crystal with $Na_2CrO_4,4H_2O$. The results of the present work indicate that lead nitrate can exist in some form which is isomorphous with either potassium nitrate or with the potassium–barium double nitrate; the most probable form is as the double salt $2KNO_3,Pb(NO_3)_2$, which has no stable existence at the ordinary temperature but might separate as a mixed crystal with $2KNO_3,Ba(NO_3)_2$.

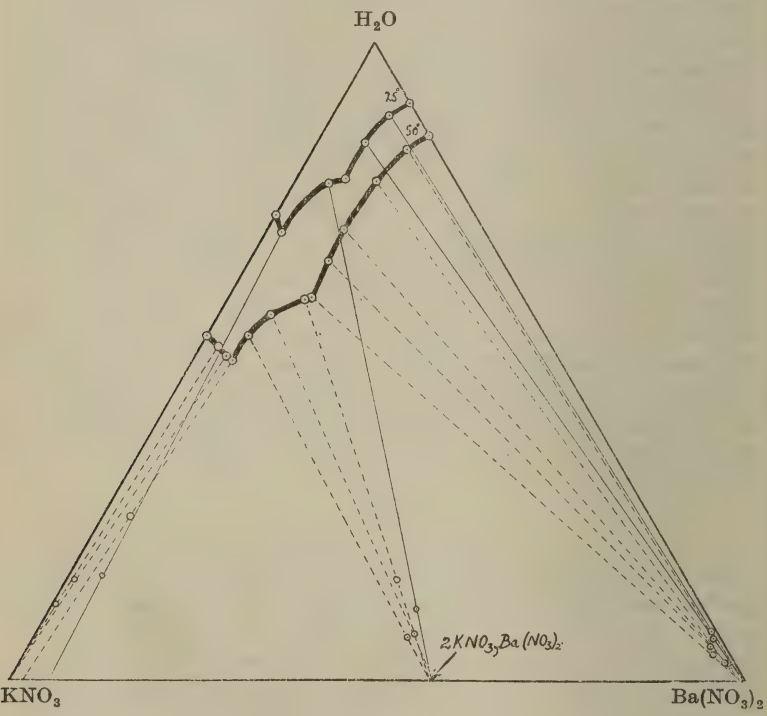
Experimental.

General Procedure.—In the case of the second of the ternary systems mentioned above, the procedure was the same as that followed in the first part of this work (Glasstone and Saunders, *loc. cit.*); for the third ternary system and the quaternary system, however, owing to the deposition of mixed crystals, it was essential that very little of the solid phase should separate, and consequently the mixed solids were made to dissolve in water at a temperature just above that at which the isotherm was being determined and the solution was stirred in a thermostat until sufficient solid for analysis had separated as the result of evaporation.

Method of Analysis.—The amounts of water in the saturated solutions and wet solids were determined by drying known weights first on the water-bath, then in an air-oven at 110°, and finally at 130°. The dry solid was then dissolved in water, made up to a known volume, and an aliquot portion taken for analysis. If the

solution contained only potassium and barium nitrates, the barium was precipitated directly as sulphate with sulphuric acid, and the barium sulphate was washed, dried, and weighed. When the solution for analysis contained lead and barium nitrates only, hydrogen sulphide was passed into the warmed solution until all the lead was precipitated; the precipitate of lead sulphide was filtered off, washed with a solution of hydrogen sulphide, and the barium in the filtrate estimated as sulphate. The amount of lead was usually

FIG. 1.



found by difference, but in several cases the sulphide was dissolved in hot dilute nitric acid and the lead estimated as sulphate by the method described in Treadwell's "Quantitative Analysis" (1919, p. 174). When the solution to be analysed contained all three nitrates, both the lead and the barium were determined by the methods described above, and the potassium was obtained by difference. The analytical method was tested beforehand on mixtures of known weights of the various nitrates and found to be quite satisfactory.

Results.—These are all given as percentages.

KNO_3–$Ba(NO_3)_2$–H_2O at 25°.

Solution.			Rest.			
KNO_3.	$Ba(NO_3)_2$.	H_2O.	KNO_3.	$Ba(NO_3)_2$.	H_2O.	Solid phase.
27·39	0·00	72·61	—	—	—	KNO_3
27·67	2·44	69·89	78·65	4·84	16·51	KNO_3 + D.S.
17·14	4·88	77·98	39·31	49·67	11·02	D.S.
*14·8	6·6	78·6	—	—	—	D.S. + $Ba(NO_3)_2$
9·13	6·57	84·30	1·18	92·26	6·56	$Ba(NO_3)_2$
3·80	7·72	88·48	1·05	91·18	7·77	,,
0·00	9·28	90·72	—	—	—	,,

D.S. refers to the double salt $2KNO_3,Ba(NO_3)_2$.
* Taken from Foote, *loc. cit.*

KNO_3–$Ba(NO_3)_2$–H_2O at 50°.

Solution.			Rest.			
KNO_3.	$Ba(NO_3)_2$.	H_2O.	KNO_3.	$Ba(NO_3)_2$.	H_2O.	Solid phase.
45·45	2·34	52·21	87·05	0·65	12·30	KNO_3
44·88	4·22	50·90	84·20	1·25	14·55	,,
44·66	5·11	50·23	74·36	3·87	21·77	KNO_3 + D.S.
40·31	5·64	54·05	42·78	50·55	6·67	D.S.
35·75	6·99	57·26	42·38	46·05	11·57	,,
30·08	10·16	59·76	41·56	50·93	7·51	,,
28·86	10·81	60·33	2·18	92·55	5·27	D.S. + $Ba(NO_3)_2$
24·14	10·43	65·43	0·02	95·39	4·59	$Ba(NO_3)_2$
18·76	10·14	71·10	2·28	93·48	4·24	,,
10·53	10·92	78·55	1·33	95·39	3·28	,,
3·93	12·73	83·34	1·07	95·85	3·08	,,
0·00	14·63	85·37	—	—	—	,,

The results obtained for this system are represented in Fig. 1.

$Pb(NO_3)_2$–$Ba(NO_3)_2$–H_2O at 25°.

Solution.			Rest.			Solid phase.	
$Pb(NO_3)_2$.	$Ba(NO_3)_2$.	H_2O.	$Pb(NO_3)_2$.	$Ba(NO_3)_2$.	H_2O.	$Pb(NO_3)_2$.	$Ba(NO_3)_2$.
34·60	1·39	64·01	81·83	11·26	6·91	87·54	12·46
31·13	2·65	66·22	66·90	18·90	14·20	76·56	23·44
22·73	4·23	73·04	38·08	56·67	5·25	39·27	60·73
16·21	5·29	78·50	—	—	—	—	—
8·96	6·66	84·38	15·06	80·02	4·92	15·44	84·56
6·26	7·31	86·43	10·15	84·28	5·57	10·42	89·58
1·63	8·64	89·73	3·44	89·54	7·02	3·59	96·41

$Pb(NO_3)_2$–$Ba(NO_3)_2$–H_2O at 50°.

Solution.			Rest.			Solid phase.	
$Pb(NO_3)_2$.	$Ba(NO_3)_2$	H_2O.	$Pb(NO_3)_2$.	$Ba(NO_3)_2$.	H_2O.	$Pb(NO_3)_2$.	$Ba(NO_3)_2$.
40·82	2·57	56·61	77·06	9·54	13·40	88·31	11·69
37·78	3·83	58·39	63·40	26·10	10·50	69·02	30·98
29·31	6·32	64·37	40·31	55·14	4·55	41·25	58·75
17·05	9·12	73·83	—	—	—	—	—
10·34	11·05	78·61	8·92	83·87	7·21	8·78	91·22
5·72	12·68	81·60	6·60	87·70	5·70	6·67	93·33

The results obtained for this system are represented in the usual manner in Fig. 2. In the columns headed "solid phase" are given

FIG. 2.

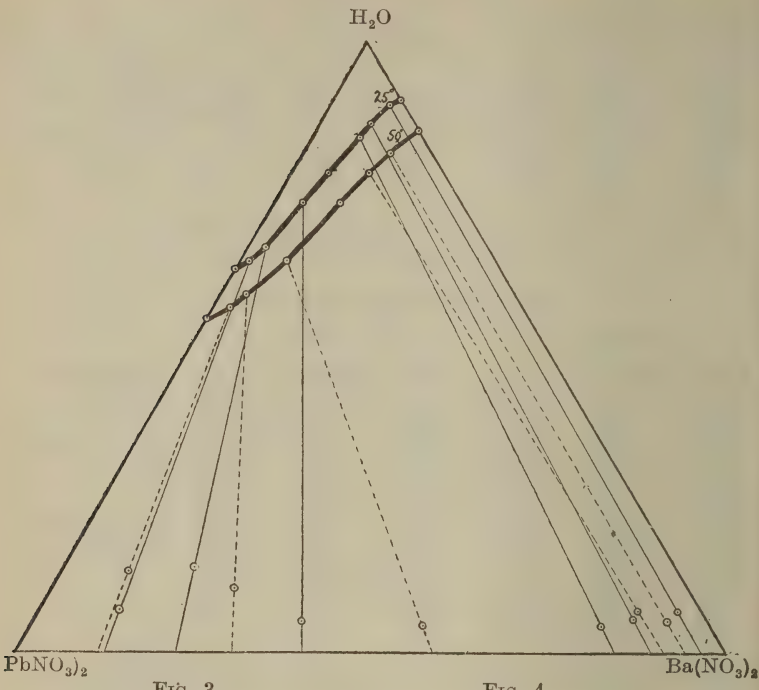
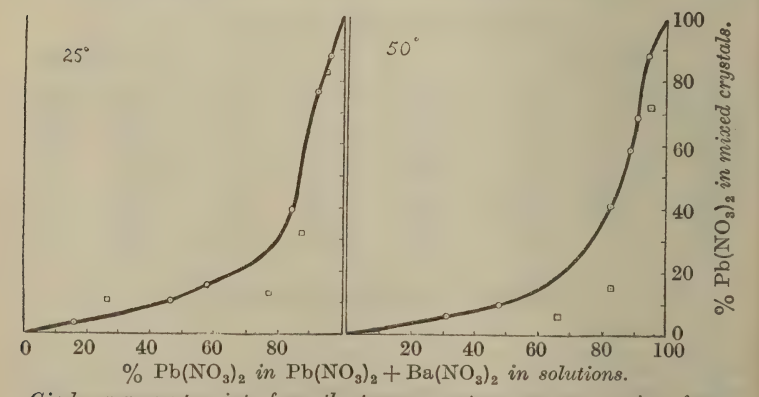


FIG. 3.

FIG. 4.



Circles represent points from the ternary system; squares, points from the quaternary system.

the compositions of the mixed crystals, which separate from the various solutions, in the dry state; these results were obtained from

the analysis of the wet solid by allowing for the amounts of salt present in the adherent mother-liquor. Fig. 3 gives the gram-percentage of lead nitrate in the mixed crystals against the gram-percentage of lead nitrate in the total salt dissolved in the solution from which the crystals separate at 25°, whilst Fig. 4 gives the corresponding curve at 50°.

KNO_3–$Pb(NO_3)_2$–$Ba(NO_3)_2$–H_2O at 25°.

Solution.				Dry solid.			
KNO_3.	$Pb(NO_3)_2$.	$Ba(NO_3)_2$.	H_2O.	KNO_3.	$Pb(NO_3)_2$.	$Ba(NO_3)_2$.	Phases.
15·26	2·12	6·05	76·57	43·23	0·10	56·67	D.S.+ M.C.
17·39	11·44	3·40	67·77	41·98	0·43	57·59	,,
15·99	13·82	4·76	65·43	43·45	0·80	55·75	,,
16·01	21·25	4·33	58·41	43·51	1·70	54·79	,,
15·65	26·59	4·06	53·70	0·88	31·36	67·76	,,
17·87	35·90	2·46	43·77	23·10	14·95	61·95	,,
23·41	37·68	2·11	36·80	23·78	38·10	38·12	,,
25·75	34·65	1·16	38·44	69·45	4·42	26·13	D.S.+ M.C.+ KNO_3
25·74	32·63	1·92	39·71	91·23	1·36	7·41	D.S.+ KNO_3
26·78	23·26	1·76	48·20	92·31	0·61	7·08	,,
27·23	15·28	2·32	55·17	96·06	0·23	3·71	,,
27·69	9·85	1·87	60·59	92·13	0·10	7·77	,,
27·74	4·95	1·92	65·39	63·28	0·30	36·42	,,
25·22	40·46	0·72	33·60	45·44	51·86	2·70	KNO_3 + M.C.
25·00	39·84	1·18	33·98	2·11	28·02	69·87	,,
25·00	38·00	1·59	35·41	10·61	76·19	13·20	,,
24·91	37·48	1·80	35·81	94·90	1·31	3·79	,,

M.C. refers to $Pb(NO_3)_2$–$Ba(NO_3)_2$ mixed crystal.

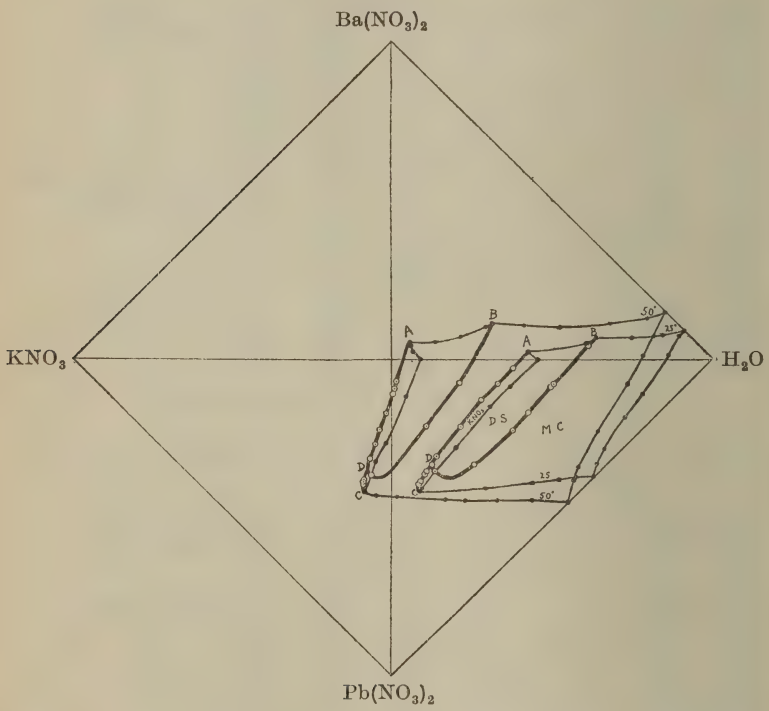
KNO_3–$Pb(NO_3)_2$–$Ba(NO_3)_2$–H_2O at 50°.

Solution.				Dry solid.			
KNO_3.	$Pb(NO_3)_2$.	$Ba(NO_3)_2$.	H_2O.	KNO_3.	$Pb(NO_3)_2$.	$Ba(NO_3)_2$.	Phases.
27·40	15·89	8·11	48·60	1·04	6·15	92·81	D.S.+ M.C.
28·28	27·00	5·68	39·04	9·41	11·94	78·65	,,
32·61	38·93	2·15	26·31	15·02	47·42	37·56	,,
35·48	33·62	2·01	28·89	91·53	1·02	7·45	D.S.+ KNO_3
36·91	29·22	2·24	31·63	92·65	0·00	7·35	,,
38·06	24·98	2·59	34·37	65·31	1·62	33·07	,,
39·43	19·96	2·85	37·76	57·61	0·94	41·45	,,
40·90	14·64	3·32	41·14	54·03	0·65	45·32	,,
41·39	13·01	3·44	42·16	71·12	0·44	28·44	,,
41·86	10·35	3·69	44·10	97·69	0·19	2·12	,,
33·25	40·88	1·02	24·85	53·25	43·15	3·60	KNO_3 + M.C.
33·41	40·19	1·51	24·89	34·54	35·58	29·88	,,
32·64	39·82	2·40	25·14	46·76	46·12	7·12	,,

The two isotherms in this quaternary system have been drawn from the above results by the method of Schreinemakers, as this was found to give the least confusing diagram, and are represented in Fig. 5. The points A, B, and C represent the composition of ternary liquids which are in equilibrium with two solid phases—potassium nitrate and double salt, double salt and lead nitrate, and potassium and lead nitrates, respectively—whilst the points on the

curves AD, BD, and CD give the composition of quaternary solutions in equilibrium with double salt and potassium nitrate, double salt and mixed crystal, and potassium nitrate and mixed crystal, respectively. The point D represents the composition of the quaternary isothermal invariant solution. The composition of the dry solid given in the above tables was obtained by calculating, from the analysis of the solutions, the amounts of the three nitrates dissolved in the water which was present in the wet solid and deducting

FIG. 5.



these from the total amounts found by the analysis of the dried residue.

An examination of the results given above for the quaternary system shows that when the two solid phases in equilibrium with saturated solution should consist only of potassium nitrate and double salt, there is also present a small amount of lead salt; the results are so consistent as to rule out the possibility of experimental error. The presence of lead has been confirmed by washing the wet solids with a little water and grinding the residue at 30—35° with a solution, containing roughly 25% of potassium nitrate and 2%

of barium nitrate, which dissolves lead nitrate very readily. The solid was then filtered off and ground up with a fresh portion of the solution; this process was repeated several times, but even after ten treatments the solid residue still contained an appreciable quantity of lead salt. These results indicate that lead nitrate in some form is separating as a mixed crystal either with potassium nitrate or else with the double salt. The most probable explanation is that the double salt $2KNO_3,Pb(NO_3)_2$, which has no stable existence alone under ordinary conditions, is separating out from solution as a mixed crystal with the barium double salt of similar formula. Other explanations are, of course, possible, but they seem to be less probable.

In order to obtain, if possible, further evidence for the existence of the double salt of lead and potassium nitrates, the results for the systems from which the potassium–barium double nitrate and mixed crystals of lead and barium nitrates separate were examined as follows. It was assumed as a first approximation that all the potassium nitrate in the solid phase was in the form of the double salt with barium nitrate, and so the amount of barium nitrate present as double salt was calculated; the residual barium nitrate was assumed to be present as mixed crystal with lead nitrate. In this way, the ratio of lead nitrate to barium nitrate in the mixed crystal was determined and compared with the ratio of these two salts in the quaternary solution. The results are given below.

25° $\frac{Pb(NO_3)_2}{Pb(NO_3)_2 + Ba(NO_3)_2}$ %.		50° $\frac{Pb(NO_3)_2}{Pb(NO_3)_2 + Ba(NO_3)_2}$ %.	
Solution.	Mixed crystal.	Solution.	Mixed crystal.
94·69	82·49	94·75	72·35
86·76	32·00	82·62	15·09
77·07	12·78	66·20	6·32
25·95	10·67		

These results have been plotted in Figs. 3 and 4 for 25° and 50° respectively for the purpose of comparison with the results for the ternary system. It is seen that for a given ratio of lead nitrate to barium nitrate in the solution the mixed crystal separating from the ternary solution contains relatively more lead than does that separating from the quaternary system; if a lead–potassium nitrate double salt had been present, then the reverse would have been expected. It is possible, however, that the presence of potassium nitrate in the solution alters the ratio of lead to barium in the mixed crystal, and so no definite conclusions can be drawn from the results.

Summary.

(1) The ternary systems KNO_3–$Ba(NO_3)_2$–H_2O and $Pb(NO_3)_2$–$Ba(NO_3)_2$–H_2O have been investigated at 25° and 50°.

(2) The quaternary system KNO_3–$Ba(NO_3)_2$–$Pb(NO_3)_2$–H_2O has been investigated at 25° and 50°.

(3) There is shown to be some evidence for the existence of a double salt, $2KNO_3,Pb(NO_3)_2$, in the form of a mixed crystal with the double salt $2KNO_3,Ba(NO_3)_2$.

UNIVERSITY COLLEGE, EXETER. [*Received, November 3rd*, 1925.]

CCCXCV.—*The Behaviour of Glucose and Certain Other Carbohydrates towards Dyestuffs and towards Potassium Ferricyanide in an Alkaline Medium.*

By EDMUND KNECHT and EVA HIBBERT.

ALTHOUGH we are well informed as to what changes take place in the dyestuff when indigo or some other dyestuff is reduced by glucose in presence of alkali, no attempts to elucidate the character of the oxidation of the glucose have hitherto been recorded. Many attempts have, however, been made to ascertain the character of the oxidation products formed by the action of Fehling's solution and of cupric hydroxide in presence of caustic alkali as well as of other inorganic oxidising agents in an alkaline medium, the results of which indicate that the reactions are of a complicated character. The most complete researches on this subject are those of Gaud (*Compt. rend.*, 1894, **119**, 604), who employed Fehling's solution as the oxidising agent and obtained formic, oxalic, tartronic, lactic, and glyceric acids, along with some catechol, and the elaborate work of Nef (*Annalen*, 1907, **357**, 214) who, using copper sulphate and a slight excess of caustic soda, obtained hexonic, trihydroxybutyric, glyceric, glycollic, formic, and carbonic acids. By means of red mercuric oxide and barium hydroxide, Herzfeld (*Annalen*, 1888, **245**, 32) obtained gluconic acid as the main product. By using sodium hypoiodite as the oxidising agent, Romijn (*Z. anal. Chem.*, 1897, **36**, 19) obtained this acid alone, and Willstätter and Schudel (*Ber.*, 1918, **51**, 780) showed that the reaction may serve for the estimation of glucose.

The authors have shown (*J. Soc. Dyers Col.*, 1925, **41**, 94) that when glucose is boiled with excess of methylene-blue in presence of caustic soda, oxidation takes place very rapidly, and to a definite degree (three atoms of oxygen to one mol. of glucose). Further work in this direction has now been carried out. Methylene-blue was not entirely suitable for the purpose on account of its great liability to undergo decomposition by the action of the alkali

(Bernthsen, *Annalen*, 1885, **230**, 73), so potassium indigotintetrasulphonate, which reacts in the same way as methylene-blue, is much more stable towards alkalis, and can be estimated volumetrically with rapidity and accuracy, was used for most of the oxidations given below. The amount of indigotin reduced was invariably equivalent to three atoms of oxygen per mol. of glucose, four atoms of oxygen per mol. of lævulose and, as might have been expected, $3\frac{1}{2}$ atoms of oxygen in the case of invert-sugar. Galactose and glucosamine hydrochloride behaved like glucose, each taking up three atoms of oxygen. Maltose was apparently hydrolysed, since the molecule ($C_{12}H_{22}O_{11} + H_2O$) reduced an amount of indigotin equivalent to six atoms of oxygen.

Thioindigodisulphonic acid (*Ber.*, 1907, **40**, 3821) gave with glucose and lævulose results identical with those obtained with potassium indigotintetrasulphonate.

Potassium ferricyanide can replace indigotin in the titration of glucose, lævulose, and glucosamine, giving identical results; the reaction is very rapid, being complete in 15 seconds. The extent of the oxidation was in the first instance determined by titrating the ferrocyanide in the cooled solution, acidified with sulphuric acid, with permanganate to the appearance of a pink colour. The result was corroborated by estimating the excess of ferricyanide by means of standard sodium hydrosulphite, with methylene-blue as indicator. Ultimately it was, however, preferred to estimate the excess ferricyanide by titration with titanous chloride in presence of a trace of ferric chloride, the disappearance of the blue colour indicating the end-point. There was a close agreement of the results in all three cases.

In view of the constancy of the results obtained with methylene-blue, potassium indigotintetrasulphonate, thioindigodisulphonic acid, and potassium ferricyanide, and the exact stoicheiometric character of the reactions, it was surmised that, in the case of glucose and galactose, the oxidation had resulted in the formation of hexane tetrahydroxy-dicarboxylic acids corresponding to saccharic and mucic acids, whilst in the case of lævulose, the oxidation would just suffice to produce a mono- and a di-carboxylic acid in equimolecular proportions. In spite of numerous attempts, it has, however, not been possible to identify any of the oxidation products. The difficulty lies mainly in the removal of the large quantity of colouring matter required to effect the oxidation; for instance, 1 g. of glucose requires more than 16 g. of potassium indigotintetrasulphonate, which will be present, after oxidation is complete, partly as such but mainly in the reduced condition. Also, through the action of the alkali, considerable isomerisation of

the oxidation products probably takes place, and these do not possess the uniformity of the product of oxidation in an acid medium.

If glucose, which is neutral to phenolphthalein, is converted into a dicarboxylic acid (or acids) during the reaction, the extent of such conversion should be measurable by titration, for the resulting acid would require two equivalents of caustic alkali for its neutralisation. On similar grounds, the acids resulting from the alkaline oxidation of lævulose should require three equivalents of alkali. It was obviously impossible to use dyestuffs as oxidants to test the validity of this reasoning. Pure potassium ferro- and ferri-cyanides are neutral to phenolphthalein, and the latter was employed as the oxidant in the experiments. In carrying out the estimations it had to be taken into consideration that potassium ferricyanide, in becoming reduced to ferrocyanide, takes up two molecules of potassium hydroxide for each atom of oxygen supplied. The results confirmed exactly the above reasoning.

It is known that, in the titration of glucose by means of Fehling's solution, the extent of the oxidation, as measured by the amount of copper reduced, is represented by rather less than $2\frac{1}{2}$ atoms of oxygen per molecule of glucose. On the other hand, it has been shown that by employing, in place of Fehling's solution, the solution of copper carbonate in potassium carbonate and bicarbonate advocated by Soldaini (*Gazzetta*, 1876, **6**, 322), the degree of oxidation is almost doubled (see also Ost, *Ber.*, 1890, **23**, 1035, 3003).* It was therefore considered possible that the use of an alkaline carbonate in the titration of glucose with indigotin might also give rise to a higher degree of oxidation. The results obtained, however, were in no way modified by substituting for the potassium hydroxide an amount of potassium carbonate and bicarbonate equivalent to that employed in the alkaline copper carbonate solution. In carrying out the titration, it is important that the substances be added in the sequence given. If the caustic potash is added to the boiling glucose solution before the indigotin, 30 seconds' boiling is sufficient to lower the result by 50% or more. This seems to be due to the conversion of some of the glucose into lactic acid (Nencki, *J. pr. Chem.*, 1881, **24**, 498). If the boiling is continued for 2 minutes, the amount of alkali neutralised corresponds exactly to the formation of two molecules of lactic acid. Lævulose behaves in this respect like glucose.

Neither lactic, saccharic, mucic, nor gluconic acid reduced

* No satisfactory explanation of this great difference in the behaviour of the two solutions has hitherto been advanced.

methylene-blue when boiled with this dyestuff in presence of caustic potash.

When kitone-blue *A*, (*p*) $SO_3Me{\cdot}C_6H_3(SO_3[o]){\cdot}C{\leqslant}^{C_6H_4{\cdot}NEt{\cdot}C_7H_7}_{C_6H_4{\cdot}NEt{\cdot}C_7H_7}$,

was substituted for methylene-blue or potassium indigotintetrasulphonate as oxidant, both glucose and lævulose took up exactly two atoms of oxygen per molecule. This would correspond to the formation of glycuronic acid from the first and of hydroxygluconic acid from the second of these carbohydrates. Superimposing an indigotin titration on the kitone-blue titration of glucose resulted in a further atom of oxygen being taken up. From its behaviour towards methylene-blue and towards indigotintetrasulphonic acid, it might have been expected that lævulose, after being oxidised with kitone-blue, would take up two more atoms of oxygen on superimposing a methylene-blue titration. Only one further atom of oxygen was taken up.

Rosinduline 2*B*, when employed as the oxidising agent, supplied only one atomic proportion of oxygen to glucose. By superimposing a methylene-blue titration, no further oxidation took place; and, although the oxidation product was not identified, this circumstance strengthens the opinion that the oxidation had resulted in the quantitative formation of gluconic acid.

Experimental.

In principle, all the titrations are carried out in the same way. A known weight of the carbohydrate is heated with a known volume of a standard solution of the oxidising dyestuff, which must be present in considerable excess, in a current of nitrogen. When the mixture boils, caustic potash is added, and the boiling continued for the time specified. The mixture is now at once acidified, and the excess of dyestuff titrated with titanous chloride in a current of carbon dioxide. The quantity of carbohydrate most suitable for a titration is 0·01—0·05 g., and the quantity of caustic potash required is about 0·5 g., or 5 c.c. of a 10% solution.

The following special points should be noted in carrying out the titrations.

Methylene-blue. A suitable strength of this dyestuff (working with a titanous chloride solution of which 1 c.c. = 0·002 g. Fe or thereabouts) is 10 g. of the medicinal product per litre. The time of boiling in presence of alkali should in no case exceed 5 seconds; beyond this limit, the methylene-blue loses strength through decomposition and the results become untrustworthy.

Potassium indigotintetrasulphonate. A suitable strength is 40 g.

of the crystallised dyestuff per litre. The procedure consists in adding to an aqueous solution of a definite weight of glucose excess of the standard indigotin solution. The mixture is boiled in a current of nitrogen, caustic soda is added, and the boiling continued for ½ minute. The mixture is then acidified with dilute sulphuric acid, excess of tartrate of soda added, and the hot solution titrated with titanous chloride until the blue colour disappears.

Ferricyanide. A suitable strength for a standard solution is 50 g. per litre. The quantity of caustic potash added should be more than sufficient to allow for the formation of ferrocyanide and for the neutralisation of the organic acids formed. The time of boiling is 15 seconds. The mixture is rapidly cooled in running water before being acidified with dilute sulphuric acid. The excess ferricyanide is then titrated with standard titanous chloride, as described. It is not necessary to employ either nitrogen or carbon dioxide.

Kitone-blue. A suitable strength is 10 g. per litre. Boiling for 30 seconds suffices to complete the oxidation, after which the solution is acidified with tartaric acid in slight excess before the excess of dyestuff is titrated with titanous chloride.

Rosinduline 2B. Strength and procedure as for kitone-blue. Rosinduline *G* also may be used for the purpose. *Crystal-scarlet* was not found suitable as an alkaline oxidising agent, the end-point not being sharp. Like the rosindulines, this dyestuff supplies one atom of oxygen to glucose.

Titration of Glycuronic Acid.—A solution of pure euxanthic acid (0·201 g.) in sulphuric acid (*d* 1·735) was diluted, boiled and filtered, and the separated euxanthone was washed so that the filtrate contained the whole of the glycuronic acid. The solution thus obtained reduced indigotin equivalent to 26·4 c.c. of $TiCl_3$ (1 c.c. $TiCl_3$ = 0·002001 g. Fe), indicating that almost exactly one atom of oxygen had been used. Expressed as percentage of glycuronic acid in euxanthic acid, the result gives 45·5% as against 45·9% calculated for $C_{19}H_{16}O_{10} + H_2O$. Almost the same result was obtained in the osazone process: 0·035 g. of the same specimen of euxanthic acid was hydrolysed with sulphuric acid as before, and the resulting glycuronic acid converted into the osazone; this required 14·4 c.c. of $TiCl_3$ (1 c.c. = 0·001924 g. Fe) (Found: 45·7% calculated on the euxanthic acid employed).

Action of Sodium Hydroxide on Glucose and Lævulose.—An aqueous solution of 0·5045 g. of glucose was boiled with 25 c.c. of *N*-sodium hydroxide for 2 minutes, and the excess of alkali then titrated with *N*-sulphuric acid and phenolphthalein. The amount of caustic soda neutralised was 5·6 c.c., which is equal

to 44·4% on the weight of the glucose (calc. for *N*-NaOH, 44·5%).

0·5115 Gram of lævulose, similarly treated, required 5·7 c.c. of *N*-sodium hydroxide, which represents 44·4% on the weight of the lævulose. In another experiment the boiling with caustic soda was continued for 5 minutes; this did not affect the result.

Acidimetric Titration of the Oxidation Products of Glucose and Lævulose.—Glucose (0·5 g.) was oxidised with 7·5 g. of potassium ferricyanide and 50 c.c. of *N*-potassium hydroxide. Titration with *N*-sulphuric acid and phenolphthalein then showed that 1·24 g. of potassium hydroxide had been neutralised in the reaction. The amount required according to the equation is 1·245 g.

On similar treatment of 0·5 g. of lævulose, 1·45 g. of potassium hydroxide were neutralised (calc., 1·40 g.).

Indigotin Titration superimposed on Kitone-blue Titration.—0·02084 Gram of glucose required kitone-blue equivalent to 13·6 c.c. of $TiCl_3$ (1 c.c. = 0·001916 g. Fe), which (for 2 atoms of oxygen supplied) corresponds to 0·02094 g. of glucose or 100·4%. In the superimposed indigotin titration, an amount of indigotin equivalent to 6·9 c.c. of $TiCl_3$ was required, corresponding (for one additional atom of oxygen) to 0·02123 g. of glucose or 101·3%.

Sugar.	Oxidant.	Sugar taken (g.).	Titre of $TiCl_3$ (1 c.c. $= - \times 10^{-4}$ g. Fe).	$TiCl_3$ (c.c.).	Sugar found (g.).	% of sugar taken.
Glucose	M	0·03956	27·42	26·7	0·03922	99·15
,, ...	I	0·0400	18·38	40·5	0·03988	99·7
,, ...	Th	0·03733	19·23	36·2	0·037286	99·8
,, ...	F	0·02029	19·23	19·7	0·02032	99·8
,, ...	R	0·0400	19·98	12·4	0·03984	99·6
,, ...	K-b	0·0200	19·98	12·5	0·020075	100·4
Lævulose	M	0·04006	20·81	48·1	0·04023	100·4
,, ...	I	0·02023	19·15	26·2	0·02016	99·7
,, ...	Th	0·0400	19·23	51·5	0·03976	99·4
,, ...	F	0·0390	19·23	50·5	0·03898	99·9
,, ...	K-b	0·0200	19·98	26·2	0·03033	100·3
Sucrose (inv.)...	M	0·0291	15·72	42·5	0·02914	100·1
,, ...	I	0·0227	20·01	25·9	0·02261	99·6
,, ...	F	0·0227	20·01	26·0	0·02269	99·9
Galactose	M	0·0388	17·24	42·0	0·03879	99·8
,, ...	I	0·03304	18·45	33·4	0·03300	99·8
Arabinose	I	0·0400	20·66	42·4	0·03911	97·8
Glucosamine hydrochloride	I	0·05232	19·23	42·3	0·05219	99·7
Glucosamine hydrochloride	F	0·02505	17·49	22·2	0·02493	99·5
Glycuronic acid in euxanthic acid	I	0·2010	20·01	26·4	0·09150	45·5

M, methylene-blue; I, potassium indigotintetrasulphonate; Th, thio-indigodisulphonic acid; F, potassium ferricyanide; R, rosinduline; K-b kitone-blue.

Various amounts of glucose with potassium indigotintetrasulphonate as oxidising agent.

Glucose taken (g.).	C.c. of $TiCl_3$ used.	Glucose found (g.).	% of glucose taken.
0·052675	50·1	0·052505	99·7
0·04214	40·2	0·042129	99·9
0·02107	20·0	0·02096	99·5
0·010535	10·1	0·010585	100·4
0·0052675	5·0	0·00524	99·5

1 C.c. $TiCl_3$ = 0·001956 g. Fe.

Various amounts of glucose with potassium ferricyanide as oxidising agent.

0·0800	65·3	0·0798	99·8
0·0500	41·0	0·0500	100·05
0·0400	32·6	0·0399	99·7
0·0198	16·2	0·0198	100·0
0·0099	8·1	0·0099	100·0

1 C.c. $TiCl_3$ = 0·002272 g. Fe.

Summary.

1. It is shown that, in an alkaline medium, glucose, lævulose, and certain other carbohydrates are oxidised to a definite degree by methylene-blue and by potassium indigotintetrasulphonate. Glucose, glucosamine, and galactose take up, under the conditions, exactly three, and lævulose four, atomic proportions of oxygen. Potassium ferricyanide can replace the dyestuffs in these estimations.

2. When boiled for two minutes with excess of caustic soda in an atmosphere of nitrogen, both glucose and lævulose neutralise an amount of alkali corresponding exactly to the formation of two molecules of lactic acid.

3. When glucose is boiled with excess of potassium ferricyanide and caustic potash, the amount of alkali neutralised (over and above that required to form potassium ferrocyanide) represents exactly three equivalents of caustic potash. In the case of lævulose, the amount of caustic potash neutralised is approximately four equivalents.

4. Glycuronic acid can be estimated quantitatively by titration with potassium indigotintetrasulphonate. The volumetric osazone titration method may also be employed for the purpose.

5. In presence of caustic alkali, glucose is also oxidised quantitatively by kitone-blue and by rosinduline. In the former case, two, and in the latter, one atomic proportion of oxygen is supplied by these dyestuffs.

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CCCXCVI.—*The Salting-out Effect. The Influence of Electrolytes on the Solubility of Iodine in Water.*

By John Stanley Carter.

The fact that the solubility of non-electrolytes in water is lowered by addition of electrolytes has attracted considerable attention, and various empirical or semi-empirical equations have been put forward to express the relation between the change in the solubility and the concentration of the electrolyte. In most of the earlier work, the latter rarely exceeded one gram-equivalent per litre, and over this range the solubility lowering is approximately proportional to the concentration of the electrolyte. Experiments in which the electrolyte concentration was varied over a wider range show, however, that this proportionality by no means holds.

Measurements of the solubility of phenol in sodium sulphate solutions (Dawson, *J. Soc. Chem. Ind.*, 1920, **39**, 151T), of the solubility of ethyl ether in sodium chloride solutions (Thorne, J., 1921, **119**, 262) and of quinol and quinone in various salt solutions (Linderstrom-Lang, *Compt. rend. Trav. Lab. Carlsberg*, 1924, **15**, 4) show that, over a considerable concentration range, the influence of electrolytes on the solubility of non-electrolytes can be expressed by the exponential formula $s = s_0e^{-kc}$, first suggested by Setschenov (*Z. physikal. Chem.*, 1889, **4**, 117), where s_0 and s denote respectively the solubilities of the non-electrolyte in water and in a salt solution, the concentration of which, expressed in terms of the volume of the solution, is represented by c, and k is a constant characteristic of the dissolved electrolyte.

In the present investigation, the validity of the exponential formula has been tested by measurements of the solubility of iodine in aqueous solutions, the concentration of which ranged up to saturation at the temperature of observation. In previous measurements (Jakowkin, *Z. physikal. Chem.*, 1896, **20**, 19; Dawson, *ibid.*, 1906, **56**, 606), in which the salting-out effect was examined by determining the partition of iodine between carbon disulphide and aqueous salt solutions, the concentration of the electrolytes was varied only between comparatively narrow limits. The numbers thus obtained are consequently of little use for the present purpose.

The experimental data now recorded have reference to the effects produced by sodium nitrate, sulphate, and dihydrogen phosphate and by nitric and sulphuric acids. These are all readily soluble in water and do not react with iodine. The salts of weak acids are generally inadmissible on account of hydrolysis, and the halogen

salts are unsuitable because of the readiness with which they form perhalogen compounds. Various other salts had to be rejected on account of their oxidising properties, which introduce difficulties in the estimation of the iodine by means of thiosulphate. Measurements were also made with sodium chloride, allowance for the effect of perhalide formation being made in a manner which will be described later.

Experimental.

Iodine and the salts employed were purified by the customary methods. Since Bray (*J. Amer. Chem. Soc.*, 1910, **32**, 932) has shown that the hydrolysis of iodine is repressed in faintly acid solution, the values of p_H for the solutions of sodium nitrate, sulphate and chloride were adjusted to 5—5·5 by the addition of small quantities of the corresponding acids.

In the determinations of solubility, every precaution was taken to ensure complete saturation, efficient filtration, and to prevent loss of iodine by volatilisation. In the experiments with nitric and sulphuric acids, the dissolved iodine was extracted from a known weight of the saturated solution by repeated shaking with carbon tetrachloride; the latter was then freed from mineral acid by shaking with dilute aqueous sodium acetate. Freshly prepared 0·01*N*-sodium thiosulphate was used for the titrations. In order to obtain solutions of sufficiently high salt concentration, the first experiments (with sodium sulphate) were made at 35°, but subsequent measurements were made at 25° and 10°.

Determinations of the solubility of iodine in water with a slight acid reaction (p_H 5) gave the following results (millimoles per litre):

At 10°	0·835	0·837	
At 25°	1·319	1·321	1·322
At 35°	1·808	1·809	

The values at 25° agree with the value, 1·320, recorded by Bray (*loc. cit.*), but are lower than that, 1·334, given by Hartley and Campbell (J., 1908, **93**, 741), which is considered by Bray to be a little too high.

In Table I the solubilities experimentally determined are compared with those calculated from the exponential equation, which was put into logarithmic form,

$$\log s = \log s_0 - k'c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the value of the constant k' being given by the slope of the line in the graph of log s–concentration.

In the application of this formula to the results obtained for the more concentrated solutions, the mode of expressing the concen-

tration of the dissolved electrolyte is a matter of great importance. The range of validity of the logarithmic formula is very much greater when the concentration of the electrolyte is referred to a fixed weight of water than it is when the concentration is expressed in terms of a fixed volume of solution. In the latter case, deviations appear when the concentration of the electrolyte reaches 2—3 gram-equivalents per litre, and the magnitude of these deviations increases continuously with the concentration of the dissolved salt.

For this reason, the concentrations of the electrolytes, c, represent the number of moles (equivalents in the case of sodium sulphate) per 1000 moles of water. The solubility of iodine is expressed in the same way, s' being the measured value and s the value calculated from equation (1). The values of s_0 at 25° and 35°, respectively, are 0·0238 and 0·0327. The ordinary weight percentage composition of the various solutions is given under "w%."

TABLE I.

Sodium Nitrate at 25°. $k' = 0{\cdot}00296$.

w %.	$s' \times 10^3$.	$s \times 10^3$.	w %.	$s' \times 10^3$.	$s \times 10^3$.	w %.	$s' \times 10^3$.	$s \times 10^3$.
5·89	22·2	21·8	25·67	14·5	14·5	39·83	9·11	9·16
11·10	20·2	19·9	29·75	12·5	12·9	44·16	7·53	7·60
15·31	18·5	18·4	35·43	10·8	10·8			

Sodium Nitrate at 35°. $k' = 0{\cdot}00243$.

1·98	32·7	32·3	15·89	26·8	26·2	50·1	10·0	9·94
3·48	32·0	31·4	29·06	20·1	20·1			
6·85	30·2	30·0	40·17	14·3	14·7			

Sodium Sulphate at 25°. $k' = 0{\cdot}0090$.

5·66	17·3	17·4	16·24	8·55	8·60	19·66	6·56	6·59
8·64	14·4	14·5						

Sodium Sulphate at 35°. $k' = 0{\cdot}0087$.

1·05	31·8	31·1	9·13	20·2	19·8	25·31	5·78	5·85
2·31	29·3	29·0	14·79	13·3	13·5	31·80	3·05	3·06
4·93	25·2	25·2	21·10	8·39	8·42	33·1	2·58	2·66

Sodium Dihydrogen Phosphate at 25°. $k' = 0{\cdot}0062$.

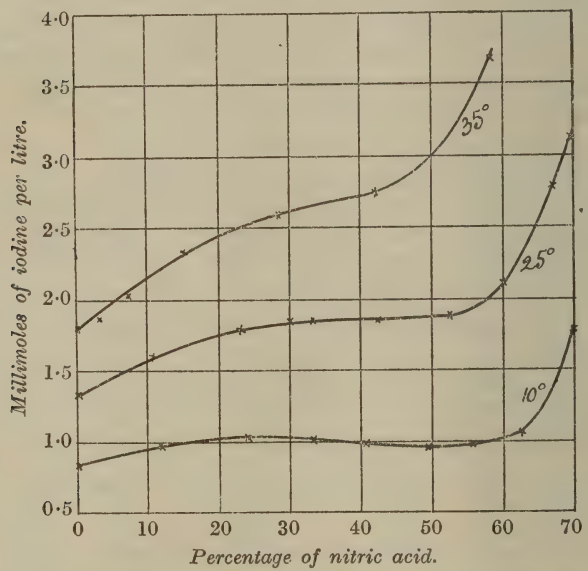
7·53	19·4	20·0	26·40	11·1	11·1	45·26	[1·8]	3·98
14·40	16·1	16·6	31·66	8·93	8·85			
20·64	13·5	13·7	41·06	[4·3]	5·35			

Comparison of the observed and the calculated solubilities of iodine shows that there is close agreement over the entire range of possible salt solutions in the case of sodium nitrate and sulphate; and also in the case of sodium dihydrogen phosphate, excepting the two most concentrated solutions, for which the measured solubilities are smaller than the calculated values. This divergence

suggests the operation of some factor other than that responsible for the normal salting-out effect. An explanation may possibly be found in the acid character of the electrolyte in this case, for, as will be seen later, the behaviour of nitric and sulphuric acids is quite different from that of the corresponding salts.

Iodine dissolved in a solution of sodium chloride exists in part as free iodine and partly in the form of a complex polyhalide. The influence of polyhalide formation is such that the solubility of iodine passes through a maximum when the concentration of the sodium chloride increases (Table II, column 2).

FIG. 1.



Solubility of iodine in aqueous solutions of nitric acid.

In order to obtain the value of k' in equation (1) for sodium chloride, it was assumed that the polyiodide equilibrium $NaCl + I_2 \rightleftarrows NaClI_2$ conforms to the requirements of the mass-law equation and that the variations in the value of the expression $[NaCl][I_2]/[NaClI_2] = a$ are due to the salting-out effect of the sodium chloride on the iodine. By plotting these values against the sodium chloride concentration and extrapolating to zero salt content, a limiting value of $a = 12{\cdot}0$ was obtained, and this was assumed to be the true value of the mass-law constant. In calculating the concentrations of free and combined iodine from this number, advantage was taken of the fact that the total salt concentration may be

substituted for [NaCl] in the mass-law equation without introducing any serious error.

TABLE II.

Sodium Chloride at 25°. $k' = 0{\cdot}00575$.

% NaCl.	Conc. of total dissolved iodine.	Conc. of combined iodine = $[NaCII_2]$.	Conc. of free iodine = s'.	s.
4·52	0·04403	0·02405	0·0200	0·0197
7·43	0·05295	0·03560	0·0174	0·0172
14·14	0·06289	0·05085	0·0121	0·0122
20·31	0·06311	0·05475	0·00835	0·00843
23·15	0·06105	0·05405	0·00700	0·00698
25·95	0·05790	0·05210	0·00580	0·00571

The close agreement between the numbers in the last two columns of Table II affords clear evidence that the salting-out effect of sodium chloride is exactly similar to that of the other salts examined when due allowance is made for the disturbing influence of polyiodide formation.

Tables III and IV contain the data for solutions of nitric and sulphuric acid. As there is no simple relation between the solubility of the iodine and the concentration of the dissolved acid, the concentration of the iodine is expressed in millimoles per litre (b).

TABLE III.

Solubility of Iodine in Nitric Acid Solutions.

10°.		25°.		35°.	
% HNO_3.	b.	% HNO_3.	b.	% HNO_3.	b.
11·80	0·969	10·91	1·60	3·31	1·87
23·88	1·035	23·16	1·79	6·50	2·04
32·35	1·020	30·05	1·85	15·50	2·33
40·82	0·985	33·62	1·86	28·72	2·60
49·57	0·952	42·28	1·85	42·63	2·75
55·82	0·962	52·77	1·89	43·13	2·73
64·30	1·08	60·36	2·10	58·34	3·68
70·00	1·78	63·81	2·36		
		67·41	2·78		
		69·65	3·12		
		72·60	3·94		

TABLE IV.

Solubility of Iodine in Sulphuric Acid Solutions at 25°.

% H_2SO_4.	b.	Colour of sat. sol.	% H_2SO_4.	b.	Colour of sat. sol.
11·87	1·02	Brown.	40·42	0·545	Brown with pink tinge.
22·72	0·820	Brown.	59·53	0·380	Pink with brown tinge.
33·25	0·615	Brown.	72·04	0·270	Pink.
			87·37	0·200	Pink.

The somewhat complicated relations exhibited by the data for solutions of nitric acid are more clearly represented in the diagram.

The curve for 35° shows that the solubility increases continuously with the concentration of the acid, but the rate of increase diminishes markedly in the middle portion of the curve. The factors which give rise to this diminution have obviously a much greater influence at lower temperatures, in that the curve for 10° shows a maximum and a minimum. At 25°, the relations are intermediate in character; the form of the curve corresponds with the behaviour expected from the results at 10° and 35°. In connexion with these results, it may be noted that solutions containing more than 60% HNO_3, although brown when viewed in bulk, have a distinctly pink shade. In sulphuric acid solutions, the solubility of iodine decreases continuously as the concentration of the acid increases from 0 to 87%, but the data do not conform at all to the requirements of the logarithmic formula which expresses the salt effects. The colour of the solutions changes gradually from brown to pink.

There is apparently no connexion between the effects observed with nitric and sulphuric acid solutions and those obtained for neutral salt solutions. If the mineral acids exert any action which is comparable with that of the salts, it is more or less completely masked by other effects which play no part in the case of the neutral salts. It seems probable that the solvent power of nitric acid for iodine is in part responsible for the complicated behaviour exhibited by nitric acid solutions.

Recent measurements (Manchot, Jahrstorper, and Zepter, *Z. anorg. Chem.*, 1924, **141**, 45) of the solubility of nitrous oxide in aqueous solutions also have shown that the influence of the free mineral acids is totally different from that of the corresponding salts.

My thanks are due to Professor H. M. Dawson for suggesting the lines of this research and for his helpful criticism and advice.

UNIVERSITY OF LEEDS. [*Received, October 30th*, 1925.]

CCCXCVII.—*The Partial Pressures of Aqueous Ethyl Alcohol.*

By HILYARD JOHN EGLINTON DOBSON.

IN connexion with work now in progress, it became necessary to have accurate data for the partial vapour pressures of ethyl alcohol at 25°, for aqueous mixtures containing up to 90% of alcohol. The system is in itself of obvious importance, yet the existing data for these properties seem to be defective. Foote and Scholes

(*J. Amer. Chem. Soc.*, 1911, **33**, 1309) obtained figures for the aqueous partial pressure which exhibit a curious break in sequence; this they ascribe to experimental error. Wrewski, working at 39·7° (*Z. physikal. Chem.*, 1912, **81**, 1), obtained similar discontinuities in the same region between 20 and 40% alcohol. The system has therefore been newly studied by the method indicated below; the results prove to be free from the anomalies hitherto prevalent, and are believed to have considerable accuracy.

Method.—The partial pressures were measured by the dynamic or "bubbling" method. This method consists essentially in measuring the mass and composition of the mixed vapour which at 25° saturates a measured volume of a chemically inert gas, and

FIG. 1.

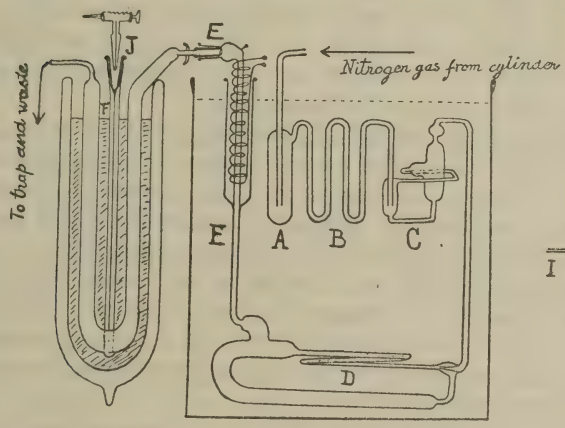


FIG. 1A.



thence calculating, with the aid of the simple gas laws, the partial pressures, or more accurately the vapour concentrations, of the two components alcohol and water. With some of the higher strengths of alcohol the mass and the composition of the vapour were measured simultaneously, but it was generally found more convenient to determine these separately for a given aqueous alcohol mixture. The determination of vapour composition is first described, and secondly the determination of the mass of vapour saturating a measured volume of gas.

Vapour Composition.—Nitrogen gas was saturated with the vapour of aqueous alcohol contained in a system of bubblers immersed in a thermostat electrically regulated at 25° ± 0·02°. The saturated vapour was then carried from the thermostat without condensation through an electrically heated tube, E (Fig. 1), to a U-tube immersed in a powerful refrigerant, and in this U-tube the vapour was quanti-

tatively condensed. The composition of the distillate was determined pyknometrically by the special means mentioned below.

Since for this purpose as much as 3 grams of liquid had to be distilled, it was essential to ensure that the change in composition of the final saturating bubbler was negligible. This was achieved by placing a slightly stronger alcohol mixture in the first bubbler, A, in which most of the evaporation occurred; the chilling due to latent heat was taken up in the long glass tube, B; whilst the remaining concentration changes were taken up by the second saturator, C, containing the same liquid as was in the final saturator, D. This was specially designed to remove all danger of spray being carried over from bursting bubbles; the absence of spray from this bubbler was proved in special experiments with highly coloured dyes.

The exposed tube, E, was covered with asbestos on which Nichrome wire was wound, and a temperature of 80—100° was maintained electrically throughout the experiment. An external glass sheath was sealed to E, so that the heating coil extended below the level of the water in the thermostat.

The U-tube proved very efficient in condensing the vapour quantitatively; and liquid air, used in many of the experiments, appeared to have little advantage over a mixture of carbon dioxide snow and ether as a refrigerant for this purpose. The U-tube was 2 feet in total length and was placed in a correspondingly large Dewar flask filled with refrigerant, and the distillation was made (generally over-night) in a current of nitrogen flowing at the rate of 1 to 3 litres per hour. Special precautions were taken, and mechanical indicators were devised which showed when any mishap had occurred. All determinations were in duplicate.

The method of sampling was as follows. When sufficient condensate had been obtained, the U-tube was removed from the Dewar flask, and the pyknometer (Fig. 1A) was fitted by the ground glass joint, J, to the sampling tube, F. When the condensate had thawed, and had been thoroughly shaken in the U-tube (to nullify fractionation), it was forced by air pressure into the bulb of the pyknometer to the mark H. The tap was then turned so as to close the bulb, and to connect the joint, J, to the side tube, I. A rubber cap was slipped over J, and the pipette was immersed in the thermostat at 25°. When equilibrium was attained, excess of alcohol was absorbed by spills of filter-paper, till the meniscus stood at the mark H. The pyknometer was now dried, and before weighing it the passage through the tap was washed out from I to J by sucking 30% alcohol through and drying the passage with a current of air.

In this way, weighings reproducible to 0·2 mg. were obtained, giving densities agreeing within less than 0·0001 unit. Densities

at 25° were used throughout for the estimation of percentage composition. This was read from the smooth curve obtained by plotting on a large scale the accurate data of Osborne and McKelvy (Landolt-Bornstein-Roth, " Tabellen," 1923 Ed., p. 448).

TABLE I.

The Vapour of Aqueous Alcohol.

Liquid. $d_4^{25°}$.	Weight % alcohol		Condensed vapour. $d_4^{25°}$.	Error of weight % figures.	Temp. of condensation of vapour.
	in liquid.	in vapour.			
0·98618	6·21	35·80	0·93990	0·03	−190°
0·97701	12·36	54·20	0·90045	0·04	−190
0·96572	20·51	66·17	0·87241	0·03	−190
0·95337	28·40	72·91	0·85634	0·01	− 80
0·94360	33·90	75·38	0·85038	0·04	−190
0·93285	39·32	77·10	0·84634	0·06	−190
0·90890	50·46	80·03	0·83903	0·02	− 80
0·89512	56·50	81·23	0·83614	0·04	−190
0·86068	71·09	84·40	0·82814	0·01	− 80
0·84392	78·07	86·20	0·82341	0·03	− 80
0·81337	90·12	91·90	0·80860	0·02	−190

The results of these determinations are in Table I, and each is the mean of two or more experiments. The maximum deviation from the mean figure for each concentration is expressed in the fifth column and shows the uncertainty in the percentage compositions. That these figures give a smooth vapour composition curve is shown in Fig. 2, in which these results are compared with the previous data of Foote and Scholes, which are here represented by crosses on a broken line.

Partial Pressures.—The apparatus used was a modification of that employed by Dobson and Masson (J., 1924, **125**, 673) in measuring the aqueous vapour pressure of hydrochloric acid. A current of nitrogen gas, saturated with the vapour of the aqueous alcohol at 25°, passed through a weighed bubbler containing about 50 g. of concentrated sulphuric acid, in which both the aqueous and the alcoholic vapours were quantitatively condensed (Masson and McEwan, *J. Soc. Chem. Ind.*, 1921, **40**, 29T). The device used for collecting the issuing gas at atmospheric pressures has been already described (Dobson, J., 1924, **125**, 1968); it materially increased the accuracy of the experiments, since it maintained in the saturator a constant total pressure, which was measured by a manometer. The importance of measuring this quantity has been emphasised by Berkeley (*Nature*, 1915, **95**, 54). Foote and Scholes were apparently able to neglect this through the arrangement of their apparatus, and on this account the method of calculation materially differs from theirs.

The volume of nitrogen, v, saturated at 25° with the vapour, is

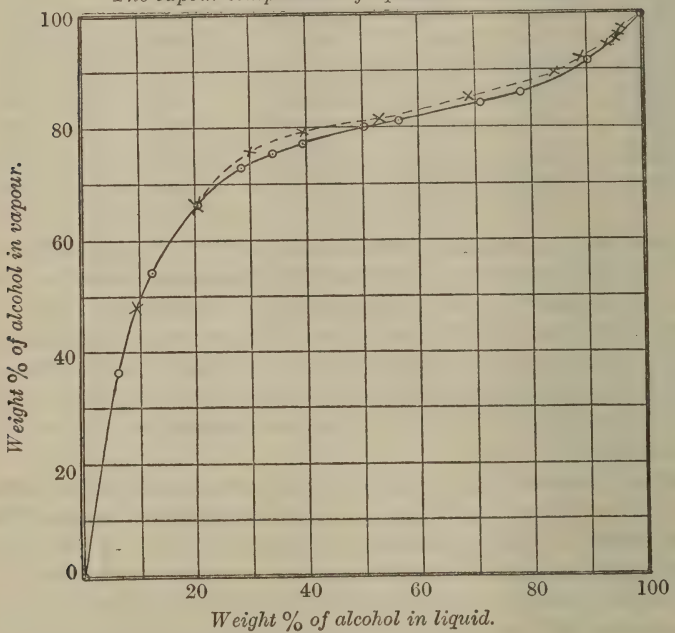
related by equation (1) to the volume, V, collected in the aspirator and measured at a temperature, $T°$ absolute, and a pressure, $B - h$, where B is the barometric height, and h the vapour pressure of water at the temperature of the aspirator, $T°$.

$$v = 298{\cdot}1V(B - h)/\{T(B_1 - p)\} \quad . \quad . \quad . \quad . \quad (1)$$

where B_1 is the total pressure in the saturator measured by the manometer, and $p = p_w + p_{alc}$, is the total vapour pressure of the mixture, which must be estimated by successive approximations.

FIG. 2.

The vapour composition of aqueous alcohol at 25°.



⊙ *Experimental points here determined.*
× *Found by Foote and Scholes* (1911, *loc. cit.*).
In no case were duplicate experiments sufficiently divergent to be shown by separate points on the scale of this figure.

The volume v is saturated at 25° by m grams of vapour, having a composition x% alcohol as given in Table I. Taking the molecular weights 18·02 and 46·06 for water and ethyl alcohol respectively, we obtain from the simple gas laws the following equations for the partial pressures :

$$p_w = \frac{3{\cdot}462\, mT(B_1 - p)}{V(B - h)} \times \frac{100 - x}{100} \quad . \quad . \quad . \quad (2)$$

$$p_{alc} = \frac{1{\cdot}354\, mT(B_1 - p)}{V(B - h)} \times \frac{x}{100} \quad . \quad . \quad . \quad . \quad (3)$$

Kendall (*J. Amer. Chem. Soc.*, 1920, **42**, 2481) has shown that saturated steam at 100° obeys van der Waals's equation when the constants a and b are deduced from the critical data. Calculation then shows that the deviation of saturated water vapour from the perfect gas laws amounts to only 0·03% at 25°. A similar calculation for saturated ethyl alcohol vapour at the same temperature shows that the gas laws hold within 0·1%. The accuracy of the equations is therefore as great as that of the experimental data.

The experimental figures are given in columns 2 to 7 of Table II. With the aid of equations 2 and 3, the partial pressures of aqueous and alcoholic vapour, p_w and p_{alc}, have been calculated and are given in columns 8 and 9.

Table II.

Experimental partial pressure results.

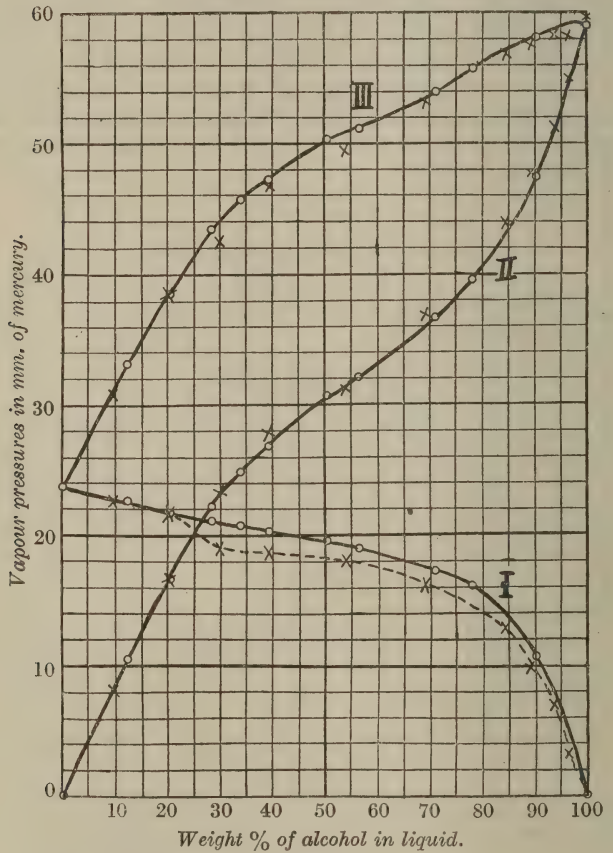
Wt. % alcohol.		Mass in grams.	Vol. litres.		Pressure in millimetres of mercury.						
							"Absolute."			"Relative."	
Liquid.	Vapour. x.	m.	V.	$T°$ abs.	$B-b$.	B_1.	p_w.	p_{alc}.	p_0.	p_w.	p_{alc}.
0	0	0·3449	15·10	293·9°	738·4	778·4	23·75	—	—	—	—
		0·4638	20·31	293·9	739·5	779·5	23·75	—	—	—	—
12·36	54·20	0·6107	12·24	292·5	742·2	764·4	22·80	10·55	—	—	—
		0·7888	16·00	293·2	740·3	763·2	22·60	10·46	23·80	22·55	10·44
		0·7454	15·10	293·9	738·4	762·1	22·71	10·51	23·75	22·71	10·51
20·51	66·17	0·9739	15·41	297·1	736·8	766·0	21·72	16·61	23·77	21·70	16·60
		1·0427	16·10	294·1	732·0	755·9	21·87	16·73	23·78	21·84	16·71
		1·0366	16·14	293·8	731·3	754·9	21·65	16·56	23·51	21·87	16·73
28·40	72·91	1·6580	20·30	285·8	749·4	768·3	21·17	22·29	23·74	21·18	22·30
		1·6316	20·33	286·7	735·8	763·3	21·11	22·22	23·71	21·15	22·26
33·90	75·38	1·4092	16·49	294·3	737·8	762·7	20·83	24·95	23·77	20·81	24·93
		1·3859	16·35	294·3	735·8	762·2	20·71	24·79	23·68	20·77	24·86
		1·2826	15·00	294·5	738·2	762·4	20·84	24·95	—	—	—
39·32	77·10	1·4590	16·37	296·7	732·2	754·1	20·24	26·65	23·45	20·50	26·99
		1·4367	16·10	297·5	731·9	754·7	20·34	26·79	—	—	—
		2·7841	31·10	294·7	741·9	761·1	20·13	26·50	23·45	20·39	26·84
		1·4955	16·15	292·0	746·5	763·0	20·55	27·07	23·73	20·56	27·09
50·46	80·03	2·0296	20·31	293·9	739·5	765·4	19·63	30·77	23·75	19·63	30·77
		2·0229	20·33	293·7	735·6	760·5	19·50	30·57	23·59	19·63	30·78
		2·0348	20·32	293·6	737·9	762·8	19·62	30·76	23·80	19·58	30·70
56·50	81·23	1·5886	15·02	290·5	747·2	760·7	18·96	32·09	23·65	19·04	32·22
		1·7458	16·36	289·0	749·7	763·3	19·04	32·22	23·86	18·95	32·07
		2·9705	28·26	292·4	732·0	748·9	19·04	32·22	—	—	—
71·09	84·40	2·3037	20·31	293·7	738·8	763·5	17·28	36·56	23·74	17·29	36·58
		2·3741	20·32	288·4	741·0	761·5	17·37	36·77	—	—	—
78·07	86·20	3·2033	26·18	291·3	745·5	764·5	16·19	39·56	23·63	16·27	39·76
		1·8569	15·30	292·7	728·2	745·4	16·08	39·28	—	—	—
90·12	91·90	1·9786	14·45	293·7	728·4	746·7	10·66	47·31	23·66	10·70	47·49
		2·1785	16·15	296·7	730·1	752·1	10·67	47·35	23·70	10·69	47·45
100	100	4·7172	29·70	292·3	746·0	759·3	—	59·01	—	—	—
Column 1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)

As in the experiments of Dobson and Masson (*loc. cit.*), a simultaneous determination was made of the vapour pressure of pure water, figures being obtained for the mass of water saturating the same volume of gas at a total pressure, B_2, measured by a second manometer. Using an equation similar to equation 2 (in which x of course becomes zero), figures were obtained for p_0, the vapour

pressure of pure water, and these constitute column (10) of Table II. These figures provide not only a measure of the accuracy of the experiment, but taking the standard mean value $p_0 = 23{\cdot}75$ mm. at

FIG. 3.

The partial pressures of aqueous alcohol at 25°.



× *Found by Foote and Scholes,* 1911.
⊙ *Experimental points here determined.*
Curve I.—The partial pressure of aqueous vapour—p_w.
Curve II.—The partial pressure of alcohol vapour—p_{alc}.
Curve III.—The total vapour pressure—p.

25°, they yield an independent measure of the vapour pressures relative to that of water at the same temperature. The "*relative*" partial pressures so obtained are given in columns 11 and 12 of Table II.

In calculating the mean values of these experiments, both "*rela-*

tive " and " *absolute* " figures were considered to be of equal value, and these mean partial pressures, together with the total vapour pressures and the vapour compositions, are given in Table III.

The vapour pressure results have been plotted graphically in Fig. 3, in which they are compared with Foote and Scholes's results.

TABLE III.

Experimental Results.

Weight % alcohol		Vapour pressures in millimetres.			Weight % alcohol		Vapour pressures in millimetres.		
in liquid.	in vapour. x.	Aqueous.	Alcoholic.	Total.	in liquid.	in vapour. x.	Aqueous.	Alcoholic.	Total.
0	0	23·75	—	23·75	50·46	80·03	19·60	30·73	50·33
6·21	35·80	—	—	—	56·50	81·23	19·01	32·16	51·17
12·36	54·20	22·67	10·50	33·17	71·09	84·40	17·31	36·64	53·95
20·51	66·17	21·78	16·66	38·44	78·07	86·20	16·18	39·53	55·71
28·40	72·19	21·15	22·27	43·42	90·12	91·90	10·68	47·40	58·08
33·90	75·38	20·79	24·90	45·69	100	100	—	59·01	59·01
39·32	77·10	20·36	26·85	47·21					

Discussion.

It appears that these experimental results differ essentially from those of Foote and Scholes in the measurement of the composition of the vapour. For, when these authors' figures for partial pressures are recalculated, using vapour compositions interpolated from the present data instead of from their own, the resulting figures for the partial pressures fall in almost every case on the smooth curves of Fig. 3. Foote and Scholes (*loc. cit.*, p. 1317) used an analytical method in which the alcohol content of the vapours was determined by combustion over copper oxide, the percentage of water in the vapour being estimated by subtracting from the total water produced, 3/2 g.-mols. for each g.-mol. of carbon dioxide weighed. In spite of the analytical care displayed by these workers, it appears that inaccuracies were liable to occur, especially where the water content of the vapour was low.

The author wishes to express his indebtedness to Professor Irvine Masson for the interest he has taken in this work, and for much helpful criticism and advice.

THE UNIVERSITY, DURHAM. [*Received, October* 31*st*, 1925.]

CCCXCVIII.—*The Methylation of the Oximes of Benzil.**

By Oscar L. Brady and Hilda M. Perry.

The methyl ethers of the oximes of benzil were investigated by Auwers and Meyer (*Ber.*, 1888, **21**, 3510) and by Dittrich (*Ber.*, 1890, **23**, 3589), both of whom prepared them by the action of methyl iodide on the sodium salts. The former obtained from α-benzildioxime two compounds corresponding in composition to the methyl ethers α_1 (m. p. 165°) and α_2 (m. p. 109—110°), and from β-benzildioxime the ethers β_1 (m. p. 72°) and β_2 (m. p. 88°). Very little seems to be known of the constitution of these ethers, although Beilstein ("Organische Chemie," 3rd ed., Vol. III, 291, 293) assigns to α_2 and β_2 the structure of *OO*-dimethyl ethers, $C_{14}H_{10}(N{\cdot}O{\cdot}CH_3)_2$. Auwers and Meyer did not think that α_1 and β_1 were true dimethyl ethers of benzildioxime.

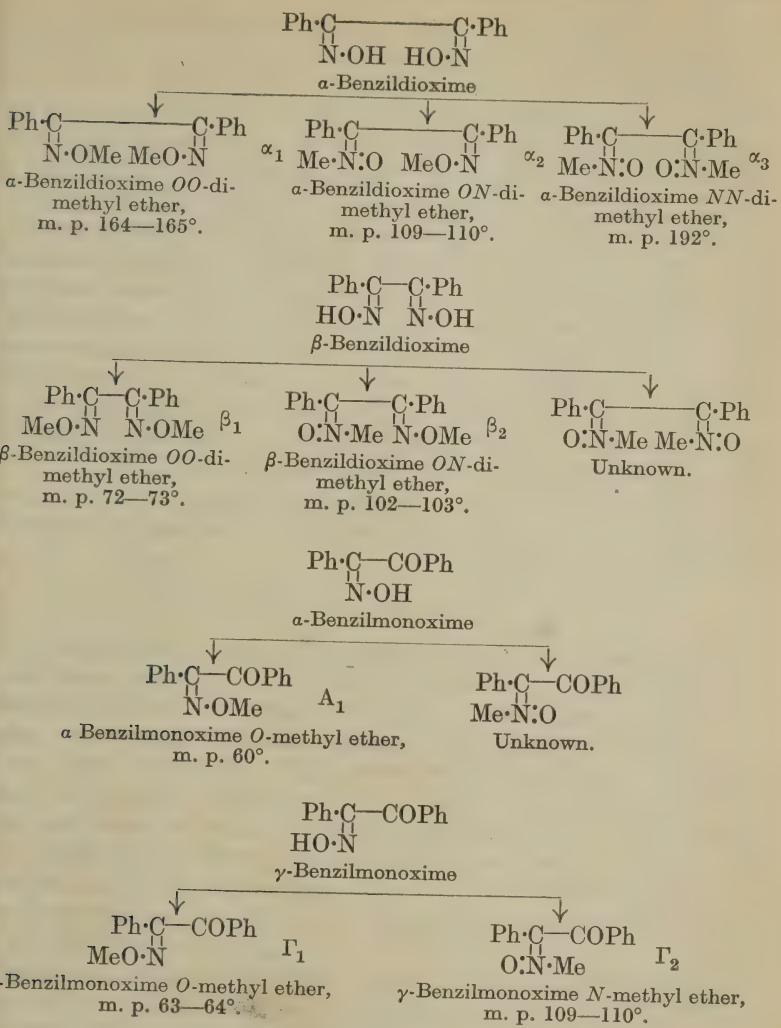
Dittrich obtained from α-benzilmonoxime a methyl ether A_1 (m. p. 62—63°) and from γ-benzilmonoxime an ether Γ_1 (m. p. 64—65°) which he regarded as *O*-ethers. Investigating the methyl ethers of the benzildioximes, he suggested that α_1 and α_2 were MeO·N:CPh·CPh:N·OMe and MeO·N:CPh·CPh·NMe, respectively.
O

From γ-benzildioxime by methylation he obtained the ether β_2, formed by isomeric change of the oxime during the reaction. On the other hand, Beilstein (*op. cit.*, 4th ed., Vol. VII, 760, 762), while accepting Dittrich's view of the constitutions of α_1 and β_1 as the result of a private communication from Auwers, assigns to α_2 and β_2 the constitutions CR(:NMeO)·CR(:NMeO).

The whole problem has now been reinvestigated, methyl sulphate being used as the methylating agent. The constitutions of the ethers have been established by heating them with hydriodic acid and determining the methyl iodide obtained from the *O*-ethers and detecting the methylamine from the *N*-ethers by Valton's method (this vol., p. 40).

On the Hantzsch-Werner theory, α-benzildioxime should give three methyl ethers, β-benzildioxime three, α-benzilmonoxime two, and γ-benzilmonoxime two. Of these ten, eight have now been characterised. The results are summarised as follows:

* The usual configurations are adopted for the oximes, and not those suggested by Meisenheimer (*Ber.*, 1921, **54**, 3206; 1924, **57**, 276, 282, 289).



γ-Benzildioxime on methylation gave an oil from which were isolated γ-benzilmonoxime *O*-methyl ether and benzil; the former was probably formed by the hydrolysis of an *ON*-dimethyl ether, and the latter from an *NN*-dimethyl ether, as the *N*-methyl compounds are hydrolysed with unusual ease.

On boiling with concentrated hydrochloric acid, α-benzildioxime *NN*-dimethyl ether gives benzil and α-benzildioxime *ON*-dimethyl ether gives γ-benzilmonoxime *O*-methyl ether, probably through α-benzilmonoxime *O*-methyl ether, the latter being converted into

the former under these conditions; whilst β-benzildioxime *ON*-dimethyl ether gives γ-benzilmonoxime *O*-methyl ether. α-Benzildioxime *OO*-dimethyl ether, on heating with concentrated hydrochloric acid in a sealed tube at 110°, gives β-benzildioxime *OO*-dimethyl ether. These results are such as would be expected and the observations of Auwers and Meyer and of Dittrich are brought into line with the usual behaviour of the ethers of the oximes: The *O*-ethers are exceptionally stable to hydrolysing agents, whereas the *N*-ethers are readily hydrolysed; the latter form hydrochlorides, the former do not; and the β-forms of the dioximes and the γ-forms of the monoximes are the most stable at high temperatures. Moreover, the formation of *O*-methylhydroxylamine, ammonia and *N*-methylhydroxylamine observed by these workers is in agreement with the results now obtained. The confusion in the literature of these compounds has thus been abolished, but the desire to obtain the complete series of ethers has been disappointed.

In the experimental part are described attempts to prepare the missing ethers by using other methylating agents and various conditions of methylation.

Experimental.*

Methylation of γ-Benzilmonoxime.—The oxime (10 g.) was dissolved in sodium hydroxide (10 g. in 120 c.c. of water and 5 c.c. of methyl alcohol) and to the filtered solution methyl sulphate (18 g.) was added in small portions, rise of temperature being avoided. The oil which separated was dissolved in ether, and light petroleum added; an oil then separated. The whole was placed in a freezing mixture and after five minutes' scratching the oil solidified. In subsequent preparations, rapid crystallisation was induced by inoculation. The solid, crystallised twice from boiling ligroin, gave *γ-benzilmonoxime N-methyl ether* in colourless needles, m. p. 109—110° (Found: N, 5·9. $C_{15}H_{13}O_2N$ requires N, 5·9%). It was sparingly soluble in ligroin or light petroleum and easily soluble in ether, benzene, or alcohol. Boiling with hydriodic acid gave no methyl iodide, but methylamine was detected by decolorising the solution with sulphur dioxide, making it alkaline with sodium hydroxide, and distilling into alcoholic 2 : 4-dinitrochlorobenzene, when 2 : 4-dinitromethylaniline was obtained (Valton, *loc. cit.*).

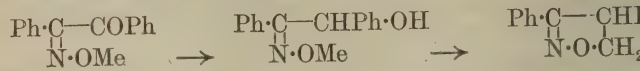
The ether–light petroleum mixture (above) was evaporated at room temperature, the residual oil dissolved in the minimum of

* It is important that all ethereal extracts should be dried before further treatment and that only anhydrous sodium sulphate should be used for this purpose.

ether, and light petroleum added, whereby a further quantity of the *N*-ether was precipitated. The filtrate on evaporation yielded an oil which solidified on treatment with a few drops of alcohol and scratching; this having been pressed on a porous tile and crystallised twice from alcohol, γ-benzilmonoxime *O*-methyl ether was obtained, m. p. 63° (Dittrich gives 64—65°).

Methoxyl determinations made to confirm the constitution of this compound gave consistently low results in presence or absence of acetic anhydride (MeO, 7·9, 8·6, 7·9. Calc., 1MeO, 13·0%). As the compound is somewhat readily volatile at 100°, a determination was carried out very slowly by heating first for an hour at 100° with the stream of carbon dioxide stopped and then at 135—140° as usual, but the result was worse (MeO, 7·4%). The heating with hydriodic acid was then carried out in a sealed tube, but a low result was again obtained (MeO, 8·2%). The compound was apparently pure, it consisted of well-formed, transparent crystals which seemed homogeneous under the microscope and remained unchanged in m. p. after crystallisation from various solvents. Dittrich obtained satisfactory analytical figures for carbon and hydrogen, and these have been confirmed (Found: C, 75·5; H, 5·5; N, 5·9. Calc., C, 75·3; H, 5·4; N, 5·9%). In view of the possibility that the substance might contain the isomeric *N*-ether the hydriodic acid solution from the methoxyl determination was examined by Valton's method (*loc. cit.*), but methylamine was not detected. Since the substance should contain some 30% of the *N*-ether to account for the low methoxyl value, and more than 0·3 g. of it was employed in the methoxyl determination, the amount of methylamine which would have been formed corresponds to 0·03 g. of methylamine hydrochloride; Valton's method will detect 0·005 g. of this compound. Moreover, no difficulty was experienced in detecting a similar amount of methylamine formed in the methoxyl determinations of the *ON*-dimethyl ethers of benzildioxime. Now γ-benzilmonoxime *O*-methyl ether is the stable isomeride, α-benzilmonoxime *O*-methyl ether passing into it on heating at 100° with concentrated hydrochloric acid. It will therefore be the first product formed when α-benzilmonoxime *O*-methyl ether and α- and β-benzildioxime *ON*-dimethyl ethers are heated with hydriodic acid (since the *N*-methylhydroxylamino-group is very easily eliminated in the last two cases); it is noteworthy that in these cases also similar low methoxyl values were obtained. If the *O*-methylhydroxylamino-groups are removed one at a time from the benzildioxime *OO*-dimethyl ethers, γ-benzilmonoxime *O*-methyl ether will be formed, and this probably accounts for the low but better methoxyl values obtained with these compounds.

If Meisenheimer's configuration (*loc. cit.*) be adopted, a possible explanation can be suggested involving reduction of the carbonyl group and ring formation by elimination of water from the resulting CH·OH and the methyl group. This point is being investigated.



Fortunately, in spite of this difficulty, the methoxyl determinations leave no doubt of the constitutions of the different ethers.

Methylation of α-Benzilmonoxime.—α-Benzilmonoxime was methylated in a similar manner as the γ-compound, and the oil which separated was removed with ether. Part of the extract on evaporation gave an oil which solidified on scratching (m. p. 54—58°); to the rest light petroleum was added until a faint turbidity was produced, and the solution left in a freezing mixture for 10 minutes, when some crystals separated (m. p. 54—58°). The mother-liquor was evaporated at room temperature; an oil was then obtained which solidified on scratching (m. p. 56—59°). No lowering of melting point occurred on mixing the various fractions, so if the second methyl derivative is formed the amount must be very small. Two crystallisations from methyl alcohol gave α-benzilmonoxime *O*-methyl ether, m. p. 58—59° (Found : MeO, 8·7, 8·5. Calc., 1MeO, 13·0%). Further search was made for the *N*-ether by distilling the mother-liquor from the first crystallisation in steam to remove the *O*-ether and extracting the residue with ether, but only a very small quantity of a red, uncrystallisable oil was obtained.

α-Benzilmonoxime *O*-methyl ether was boiled for 30 minutes under reflux with concentrated hydrochloric acid. The γ-benzilmonoxime *O*-methyl ether obtained on diluting the solution and extracting with ether was identified by the method of mixed melting points.

Preparation of α-Benzildioxime.—This oxime is best prepared by dissolving sodium hydroxide (80 g.) in water (500 c.c.) and adding, with cooling, a solution of hydroxylamine hydrochloride (40 g. in 100 c.c. of water) followed by finely powdered benzil (50 g.) and alcohol (25 c.c.). After 3 days, the small amount of unchanged benzil was filtered off and the oxime precipitated with carbon dioxide and extracted three times with boiling alcohol, in which the α-dioxime is almost insoluble. The residue melted at 230° and was considered sufficiently pure.

Methylation of α-Benzildioxime.—The oxime (10 g.) was dissolved in sodium hydroxide (30 g. in 200 c.c. of water) with the addition of a little methyl alcohol (5 c.c.). To the filtered solution, methyl

sulphate (42 g.) was added in small portions with shaking and cooling. An oil separated which slowly became pasty; this was collected and treated with a small quantity of ether, when a solid remained undissolved, m. p. 162°. Two crystallisations from alcohol gave a fine, crystalline compound, m. p. 165—166°; further crystallisation from alcohol did not raise the melting point. In a Zeisel estimation, silver iodide was produced in amount corresponding to 6·2% of OEt (Half a molecule of alcohol of crystallisation requires OEt, 7·7%); but the production of silver iodide may be due to contamination with *O*-methyl ether. The substance on crystallising three times from benzene gave large, colourless crystals, m. p. 185° (Found: N, 9·4; loss at 100°, 12·7. $C_{16}H_{16}O_2N_2,\frac{1}{2}C_6H_6$ requires N, 9·1; loss, 12·7%). On heating for 3 hours at 100°, the crystals became opaque and *α-benzildioxime* NN-*dimethyl ether* was obtained, m. p. 192° (decomp.) (Found: N, 10·5. $C_{16}H_{16}O_2N_2$ requires N, 10·4%). Neither of these compounds gave any alkyl iodide on heating with hydriodic acid. The association of solvent of crystallisation was not unexpected in view of the general tendency of the *N*-ethers of the aldoximes to separate with water of crystallisation. The *NN*-dimethyl ether is sparingly soluble in all ordinary solvents; it dissolves in concentrated hydrochloric acid in the cold and on boiling the solution benzil is formed.

The alkaline solution from the methylation was extracted with ether, and the extract added to the ether washings obtained in the preparation of the above compound. After removal of the solvent at room temperature an oil containing crystals of the *NN*-dimethyl compound was obtained. The oil was decanted off, the crystals were washed with a little alcohol, and the washings added to the oil. The solution so obtained was evaporated somewhat and concentrated hydrochloric acid added drop by drop until the whole consisted of a pasty mass, which was sucked as dry as possible. The hydrochloride was washed several times with concentrated hydrochloric acid and finally with warm ether, the ether washings being retained (A). The solid was decomposed with concentrated aqueous ammonia; a pasty mass was then formed which slowly solidified. Crystallised three times from light petroleum, it gave α-benzildioxime *NO*-dimethyl ether, m. p. 109°. This is apparently the compound, m. p. 109—110°, described by Auwers and Meyer (*loc. cit.*) (Found: MeO, 9·0, 9·4. Calc., 1MeO, 11·6%). Methylamine was detected in the hydriodic acid after the methoxyl determination.

α-Benzildioxime *NO*-dimethyl ether was boiled with concentrated hydrochloric acid for 30 minutes, and the mixture was diluted, and extracted with ether. Removal of the solvent gave an oil

from which crystals separated. After two crystallisations from alcohol, these proved to be γ-benzilmonoxime *O*-methyl ether, the :N(CH$_3$):O group having been removed and the *O*-ether of the α-monoxime converted into that of the γ-monoxime, a change which has been shown to occur under the conditions of the experiment.

The ether washings from the hydrochloride (A) were evaporated and the residue was distilled in steam. The small amount of oil which volatilised partly solidified on keeping, and the solid on crystallisation from dilute alcohol gave α-benzilmonoxime *O*-methyl ether, formed probably by the hydrolysis of the *NO*-dimethyl ether; no *OO*-dimethyl ether could be isolated and little if any of this compound appears to be formed under these conditions of methylation.

Auwers and Meyer apparently obtained the *OO*-dimethyl ether by the action of methyl iodide on the sodium salt of the oxime, but some doubt existed whether their compound, m. p. 165°, was actually the *OO*-dimethyl ether or the *NN*-dimethyl ether containing alcohol of crystallisation (m. p. 165°). A methylation with methyl iodide was carried out, a simpler technique than that of Auwers and Meyer being used; α-benzildioxime *OO*-dimethyl ether, m. p. 161°, and α-benzildioxime *NO*-dimethyl ether were obtained, but no *NN*-dimethyl ether.

A better method of obtaining α-benzildioxime *OO*-dimethyl ether consisted in mixing α-benzildioxime (2 g.) with dry silver oxide (2 g.) and methyl iodide (2·3 g.), diluting with dry ether, and heating under reflux for 2 hours. The mixture was filtered and the residue extracted twice with hot ether; on cooling, a solid separated from the filtrate. The solvent was evaporated at room temperature, leaving a solid and a small quantity of oil. The solid was crystallised three times from acetone and the α-benzildioxime *OO*-dimethyl ether described by Auwers and Meyer was thus obtained, m. p. 163—164° (Found: MeO, 18·8. Calc., 2MeO, 23·1%). This was identical with the somewhat less pure product (m. p. 161°) obtained above. The hydriodic acid solution from the methoxyl determination gave no methylamine when tested by the method described above.

Heated in a sealed tube with concentrated hydrochloric acid for 10 hours, α-benzildioxime *OO*-dimethyl either gave an oil; this solidified on scratching and after crystallising from alcohol was identified as β-benzildioxime *OO*-dimethyl ether. The observation of Auwers and Meyer was thus confirmed.

Preparation of β-*Benzildioxime.*—A much more satisfactory method of preparing β-benzildioxime than that described in the literature consists in dissolving α-benzildioxime in the minimum of freshly distilled boiling aniline; on cooling, β-benzildioxime con-

taining aniline of crystallisation separates. The crystals are sucked as dry as possible, washed with dilute hydrochloric acid, which removes the aniline of crystallisation, then with water, and crystallised twice from alcohol, when the pure β-dioxime is obtained.

Methylation of β-Benzildioxime.—β-Benzildioxime was methylated with methyl sulphate in a similar manner as the α-compound, and the oil obtained was extracted with as little ether as possible. The extract was washed several times with 0·2*N*-hydrochloric acid (to remove a trace of a basic compound which is simultaneously formed), dried, and saturated with dry hydrogen chloride; an oily hydrochloride then separated. The ether was decanted and light petroleum added. The additional hydrochloride thus obtained was added to the previous material and the whole was washed twice with small quantities of ether; the washings were added to the main bulk of the ether solution (B). The hydrochloride was decomposed with concentrated aqueous ammonia. The oil thus obtained was washed with water by decantation and left in an evacuated desiccator over solid sodium hydroxide. It slowly became very viscous, and after treatment with ligroin and 10 minutes' scratching it became pasty and finally solid (m. p. 83—89°). The ligroin washings, when allowed partly to evaporate at room temperature, deposited crystals (m. p. 88—90°). The solid (m. p. 83—89°) was heated with ligroin until it was on the point of melting, and the solution was then decanted and inoculated with a crystal of the above solid (m. p. 88—90°). This treatment was repeated with the residual semi-solid material until only a small quantity of dark oil remained. The extracts deposited an oil which solidified on keeping over-night. Fine needles projected from the solidified oil, and these melted at 90—92° and seemed to be identical with the compound, m. p. 88—89°, described by Auwers and Meyer. On keeping for some time, however, they became opaque and then melted at 102—103°. The solidified oil on crystallisation from ligroin gave the same product, m. p. 102—103°, which was β-benzildioxime *NO*-dimethyl ether (Found: MeO, 10·3. Calc., 1MeO, 11·6%). Methylamine was detected as before in the hydriodic acid from the methoxyl determination. When β-benzildioxime *NO*-dimethyl ether was heated with concentrated hydrochloric acid for ½ hour under reflux, and the mixture was cooled, diluted, and extracted with chloroform, an oil was obtained which partly solidified on cooling in ice and scratching. The solid, after purification, was found to be γ-benzilmonoxime *O*-methyl ether.

The ether–light petroleum solution (B) was evaporated at room temperature, and the solid obtained, after being freed from oil, was crystallised four times from alcohol; β-benzildioxime

OO-di-methyl ether was thus obtained, m. p. 72—73° (Found : MeO, 21·4. Calc., 2MeO, 23·1%). No methylamine was detected in the hydriodic acid residues. Methylation with methyl iodide and sodium methoxide as described by Auwers and Meyer gave the *NO*-dimethyl ether and the *OO*-dimethyl ether as above.

Methylation of γ-Benzildioxime.—The γ-dioxime was suspended in sodium hydroxide (15 g. in 100 c.c.), and methyl alcohol (5 c.c.) added, followed by methyl sulphate (21 g.) in small portions with cooling. The oil which separated was removed with ether, and the extract was washed with 0·2*N*-hydrochloric acid and treated with excess of light petroleum, which precipitated an oil (C). The mother-liquor was evaporated, the oil taken up with a little ether, and light petroleum again added; an oil (D) was precipitated. On decanting the solution and evaporating, an oil was obtained which solidified on keeping in an evacuated desiccator for some days. This solid, after crystallising twice from methyl alcohol, was found to be γ-benzilmonoxime *O*-methyl ether. The oil (C), on keeping in an evacuated desiccator for some time, partly solidified. It was then pressed on a porous tile, and the yellow solid crystallised from ligroin and from acetone and water, when benzil was obtained. The oil (D), on keeping, deposited crystals of γ-benzilmonoxime *O*-methyl ether, but all attempts to obtain a solid from the remaining oil were unsuccessful. The formation of benzil and γ-benzilmonoxime *O*-methyl ether suggests that *NN*- and *NO*-dimethyl ethers of γ-benzildioxime are formed, but are very readily hydrolysed. γ-Benzildioxime was boiled in ether with methyl iodide and dry silver oxide, and the solution was extracted with 2*N*-sodium hydroxide to remove unchanged oxime and evaporated. On keeping, the oil obtained deposited a few crystals (m. p. 145—157°), insufficient for further purification. All attempts to obtain a solid from the rest of the oil were unsuccessful.

Attempts to Prepare α-Benzilmonoxime N-Methyl Ether and β-Benzildioxime NN-Dimethyl Ether.—α-Benzilmonoxime was treated with methyl sulphate and with methyl iodide without other addition and also in ether with diazomethane. The dry sodium salt of α-benzilmonoxime was boiled with ether and methyl iodide, and benzil was treated with β-methylhydroxylamine under various conditions. None of these methods met with success. Attempts were also made to methylate β-benzildioxime with methyl sulphate and with methyl iodide without other addition, and in dry acetone solution, but no change was observed.

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CCCXCIX.—*Studies of Dynamic Isomerism. Part XX. Amphoteric Solvents as Catalysts for the Mutarotation of the Sugars.*

By Thomas Martin Lowry and Irvine John Faulkner.

1. In the preceding paper of this series (this vol., p. 1385), evidence was adduced to show that the mutarotation of the sugars is not due to a mere spontaneous tautomeric change, involving only the molecules of the sugar itself, but to a molecular rearrangement in

Fig. 1.

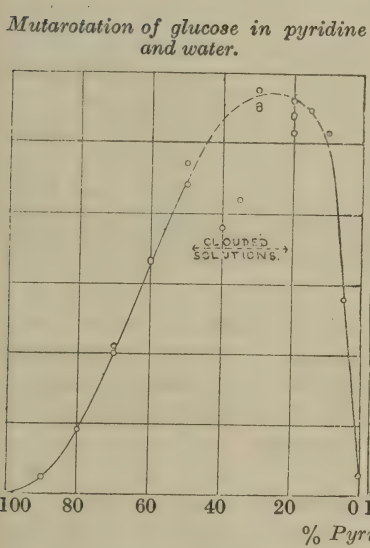
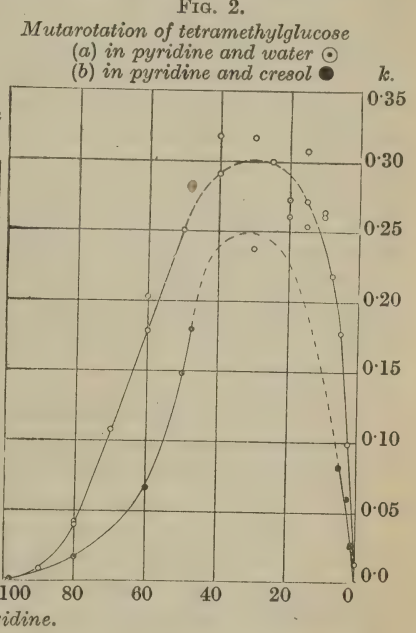


Fig. 2.



which other constituents of the solution also play an essential part. Of the constituents which interact catalytically with the sugar to bring about this rearrangement, water is the most important, since it was already obvious in 1904, from Irvine's work on the methylated sugars, that the mutarotation is retarded enormously, and in some cases may be almost stopped, by working in non-aqueous solvents. The opinion was therefore expressed (J., **85**, 1566) that all the data then available could be interpreted by attributing the mutarotation to a process of "hydrocatalysis" of the sugar.

At that time, only one assertion could be made in reference to

the mechanism of this hydrocatalysis, namely, that, since glucose hydrate exhibits just the same mutarotation as glucose itself, the change of structure which causes the changes of rotatory power could not take place during the initial hydration of the sugar, but must occur at some subsequent stage, *e.g.*, by a molecular rearrangement or isomeric change in the hydrated sugar. A further consideration of the mechanism of mutarotation (this vol., p. 1371), especially in comparison with the mechanism of hydrolysis, led, however, to a much more definite suggestion, namely, that water probably acted as a catalyst for mutarotation in virtue of the fact that it possesses both acidic and basic properties, and that, in general, the essential condition for the mutarotation of a sugar is that the solvent should possess amphoteric properties. This conclusion has the advantage of providing an explanation of the well-known fact that acids and bases produce even higher velocities of mutarotation than water alone, and of the further fact (which was discovered in the course of our own experiments) that pyridine, which is a powerful catalyst in the presence of water, is not a catalyst at all for the mutarotation of tetramethyl glucose when used in the absence of water.

2. The experiments described in the present paper had their origin in the conception of the mechanism of mutarotation which is outlined above. The most important results of the experiments are to show :

(i) That pyridine, which is inactive when dry, gives, when mixed with about twice its weight of water, a maximum velocity of mutarotation which is about twenty times as great as the velocity for solutions of the same sugars (glucose and tetramethyl glucose) in pure water.

(ii) That cresol, like pyridine, has no appreciable catalytic properties when water is not present, showing that acids and bases may alike be rendered ineffective if used in the absence of water.

(iii) That mixtures of cresol and pyridine, each sufficiently dry to give only a negligible velocity of mutarotation, when mixed in the proportion of about 2 parts of cresol to 1 part of pyridine, are again about *twenty* times as active as water in promoting the mutarotation of tetramethyl glucose.

It is, of course, possible to argue that *perfectly* dry pyridine and *perfectly* dry cresol would be incapable of producing mutarotation; but this criticism, even if it could be vindicated by experiments on the effect of extreme drying, would not affect the present discussion, since it is clear that a mixture of pyridine

and cresol is able to do what neither solvent can do by itself, namely, to give a velocity of mutarotation which is far greater than in a solvent containing 100% of water. In other words, if a trace of water is essential (as it may be even in order to enable the acid and base to interact to form an unstable salt),* the intense activity of the mixed solvent is due to its pronounced amphoteric character, and not to a direct catalytic action upon the sugar of any minute trace of water which it may contain.

3. It is interesting to notice the theoretical conclusions which follow from the experimental facts thus established, namely, (i) that (just as in the case of nitrocamphor) it is impossible for a proton to wander directly from one position to another within the molecule of the sugar, and (ii) that in order to effect this transfer, it is necessary to provide a medium into which a proton can escape from the sugar, and from which a proton can be provided to replace the proton thus lost by the sugar.

These conclusions are supported by the fact that the only substances which are now known to act as catalysts for the mutarotation of the sugars are those which possess either acidic or basic properties, or both. Oxygenated solvents such as acetone and ethyl acetate, even when used in presence of water, retard rather than accelerate the mutarotation; and even their "polar" character and relatively high dielectric constants do not enable them to develop any catalytic activity. The mechanism of mutarotation suggested above, which involves an interchange of protons between the sugar and the medium (just as in the interaction of an acid and a base) appears therefore to be the only one which is in accord with the experimental facts, and no alternative mechanism is yet known which can replace it.

Experimental.

4. The *sugars* were the same samples as those used in Part XIX. The *solvents* used were as follows: (i) Air-free distilled water. (ii) *Pyridine* (B.D.H. "Extra Pure") shaken twice with quicklime for 24 hours and distilled, twice shaken with barium oxide and twice fractionated, giving about 800 c.c. boiling from 114·8° to 115·2° (corr.) from about 1 litre. The sample gave a residual velocity of mutarotation of tetramethyl glucose not greater than 0·0004 in minute-units. (iii) *o-Cresol* (B.D.H., "for cineol-determinations") from a sealed flask was distilled immediately before use; when liquefied by the addition of a little benzene, and used

* The melting-point curve for pyridine (m. p. −41°) and *o*-cresol (m. p. 30°) rises to a maximum at +1°, in an equimolecular mixture of the acid and base (Bramley, J., 1916, **109**, 476).

as a solvent for tetramethyl glucose, it gave an arrest of mutarotation during a period of 6 hours, followed by a slow change with a velocity coefficient of about 0·0005. m-*Cresol* (B.D.H., specially prepared) was redistilled and gave a velocity coefficient of 0·0003 only.

5. *Mutarotation-curves* were plotted as follows: One gram of sugar was weighed out in a 20 c.c. flask, and the mixed solvent, previously made up by weight in another vessel, was added at zero time. The solution was transferred quickly to an air-dried polarimeter tube (2 dcm.), and readings were taken as soon as possible, namely, about 2 minutes from zero time in the case of water and pyridine, but about 5 minutes in the case of solutions rich in cresol, which were much more viscous.

6. *The experimental results* are summarised in Tables I, II,

TABLE I.

Mutarotation of Glucose in mixtures of Pyridine and Water at 20°.

% H_2O.	k.*
100	0·015
95	0·140
90	*0·258* †
85	*0·274*
80	*0·282, 0·272, 0·269, 0·258*
70	*0·225, 0·277, 0·288*
65	*0·210*
60	*0·190*
50	*0·221, 0·236*
40	0·166, 0·168
30	0·106, 0·100
20	0·046
10	0·012
0	0·0008

TABLE II.

Mutarotation of Tetramethyl Glucose in mixtures of Pyridine and Water at 20°.

% H_2O.	k.
100	0·0128
97·5	0·099
95	0·177
92·5	*0·219*
90	*0·264, 0·261*
85	*0·272, 0·254*
80	*0·267, 0·273*
75	*0·300*
70	*0·317, 0·238*
60	*0·318, 0·291*
50	*0·251*
40	*0·203, 0·179*
30	0·108
20	0·040, 0·042
10	0·0088
0	0·0003

TABLE III.

Mutarotation of Tetramethyl Glucose in mixtures of Cresol and Pyridine at 20°.

% Cresol.	k.
100 ‡	0·0003
99 ‡	0·027
97·5 ‡	0·060
95 ‡	0·082
92·5 to 55·0	Mutarotation too rapid for measurement.
52·5	0·180
49·9	0·148
40·4	0·067
21·1	0·0168
1·62	0·0013
0	0·0003

* $k = 1/t \,.\, \{\log (a_0 - a_\infty) - \log (a_t - a_\infty)\}$. In calculating this coefficient the time was always expressed in *minutes*.

† Values shown in italics correspond with a half-change period of less than 3 minutes and are not regarded as trustworthy.

‡ *m*-Cresol was used for these four solutions, as *o*-cresol is solid at these concentrations.

and III, and are represented graphically in Figs. 1 and 2. The individual readings have not been reproduced. A complete mutarotation-curve is therefore represented by a single monomolecular coefficient § in the tables, and by a single point on the curves.

§ The evidence for the monomolecular character of the curves will be discussed later in another paper.

Even under the most favourable conditions, the fastest mutarotations for which fairly trustworthy data can be given correspond with a velocity coefficient of less than 0·2, since this velocity coefficient already corresponds with a half-change period of only 2·3 minutes. Values greater than this are therefore shown in italics in the tables and are indicated only by a dotted line in Figs. 1 and 2. In the case of glucose, the mixtures which gave the highest velocities also gave cloudy solutions, which were difficult to read; but the general course of the curve can be inferred fairly accurately from the velocity coefficients for stronger and weaker solutions, for which much more concordant values were obtained. The mixtures rich in cresol suffered from the two-fold disadvantage that they were very viscous and showed only a relatively small change of rotatory power; the velocity–concentration curve for pyridine–cresol mixtures therefore includes a longer dotted section than the two curves for mixtures of pyridine and water.

We desire to thank the Department of Scientific and Industrial Research for a maintenance grant to one of us (I. J. F.) during the period in which this research was carried out.

University Chemical Laboratory,
Cambridge. [*Received, November 2nd,* 1925.]

CCCC.—*Reactions of Organic Thiosulphates.*

By Henry Bell Footner and Samuel Smiles.

Abundant evidence is available showing the instability of the disulphoxides, which are to be regarded as containing the thiol-sulphonate structure ·S·SO_2· (this vol., p. 224), and the ease with which their sulphur chain may be ruptured. To ascertain whether this type of reaction is exhibited by the thiosulphonate group under other structural conditions, the organic sodium thiosulphates, which, owing to the work of Price and Twiss (J., 1907, **91**, 2021), may be confidently assumed to have the thiol-sulphate structure, RS·SO_2·ONa, have been examined. In aqueous solution, these substances are very readily decomposed by sodium mercaptides and by alkali cyanide. The former reagent quickly yields at the ordinary temperature sodium sulphite and an insoluble product composed of a disulphide or a mixture of disulphides, according to the mercaptide used,

$$RS{\cdot}SO_3Na + NaSR' = RS{\cdot}SR' + Na_2SO_3.$$

When R and R′ are the same, this product is homogeneous and consists of a symmetrical disulphide, but when they are

dissimilar it is in most cases a mixture of the two possible symmetrical disulphides; only in a few instances has the unsymmetrical disulphide been isolated. This behaviour is closely parallel to that of the disulphoxides (J., 1924, **125**, 176),

$$RS{\cdot}SO_2R + R'SNa = RS{\cdot}SR' + RSO_2Na,$$

and the formation of the mixture of symmetrical disulphides is adequately explained by the secondary reaction of the mercaptide with disulphide (Lecher, *Ber.*, 1920, **53**, 591) :

$$RS{\cdot}SR' + NaSR \rightleftharpoons RS{\cdot}SR + R'SNa.$$

The organic thiosulphates are also quickly decomposed by aqueous alkali cyanide, more than 90% reacting thus :

$$RS{\cdot}SO_3Na + NaCN = RSCN + Na_2SO_3.$$

The products are almost pure and, the yields being excellent, the method is well adapted to the preparation of thiocyanates when the corresponding thiosulphates are available. According to unpublished experiments, the disulphoxides behave in a similar manner,

$$RS{\cdot}SO_2R + NaCN = RSO_2Na + RSCN,$$

but are much less reactive.

The interaction of mercaptans and di-*p*-toluenesulphonyl sulphide (Tröger, *J. pr. Chem.*, 1899, **60**, 117) has also been examined with similar results,

$$(C_7H_7{\cdot}SO_2)_2S + 2RSNa = C_7H_7{\cdot}SO_2{\cdot}SNa + C_7H_7{\cdot}SO_2Na + (RS)_2,$$

the sulphur chain being ruptured with formation of sulphinate and thiosulphonate together with the disulphide corresponding to the mercaptan used.

According, then, to these experiments and others previously made with disulphoxides, the characteristic reactions of the thiolsulphone group in substances of the type $RS{\cdot}SO_2{\cdot}X$ are mainly due to instability of the dithio-system; this group is readily split by alkali mercaptides and with varying ease by other reagents, the activity depending on the character of the group X.

Experiments have also been made with the polythionates. Sodium dithionate is not attacked by alkali mercaptides, but the tri- and tetra-thionates are rapidly decomposed, the disulphide being formed in both cases. The trithionate is resolved into sulphite and thiosulphate, and the tetrathionate into thiosulphate. The completed reactions,

$$Na_2S_3O_6 + 2RSNa = (RS)_2 + Na_2SO_3 + Na_2S_2O_3$$
$$Na_2S_4O_6 + 2RSNa = (RS)_2 + 2Na_2S_2O_3,$$

may be regarded as analogous to the reduction of these substances by sodium amalgam. Strictly quantitative measurements have not

been made, but more than 90% of the materials undergo the reactions indicated. Whilst the constitution of the polythionates is undetermined nothing further can be said of the nature of these reactions but, bearing in mind the known behaviour of mercaptides with the dithio and thiolsulphone systems, the processes are, in the authors' opinion, adequately explained by the structures proposed by Mendeléev for the polythionates. In this connexion, the close resemblance of the behaviour of the trithionate to that of ditoluenesulphonyl sulphide is significant.

Experimental.

Reaction of Organic Thiosulphates with Sodium Mercaptides.—The benzyl and *p*-nitrobenzyl thiosulphates used were prepared by Price and Twiss's method (*loc. cit.*) and the 9-anthryl thiosulphate by Friedländer's (*Ber.*, 1922, **55**, 3969). The sodium mercaptide (1 mol.) and the thiosulphate (1 mol.) reacted rapidly in aqueous solution at the ordinary temperature. After ½ hour, the solution was neutral and contained sulphite with at the most only traces of sulphate. The yield of the precipitated disulphides generally exceeded 95%. The results from six of the cases examined are in the following table :

Mercaptan.	Thiosulphate.	Products.
Benzyl.	Benzyl.	Benzyl disulphide, 99%.
2-Nitrophenyl.	Benzyl.	Benzyl 2-nitrophenyl disulphide, 99%.
9-Anthryl.	Benzyl.	Dianthryl, dibenzyl, and anthryl benzyl disulphides.
2-Nitrophenyl.	4-Nitrobenzyl.	2-Nitrophenyl and 4-nitrobenzyl disulphides.
2 : 5-Dichlorophenyl.	9-Anthryl.	Dianthryl and tetrachlorodiphenyl disulphides.
2-Nitrophenyl.	9-Anthryl.	2-Nitrophenyl and anthryl disulphides.

The symmetrical disulphides named have been previously described.

Benzyl 2-nitrophenyl disulphide separated from alcohol in yellow needles, m. p. 54° (Found : N, 5·4; S, 23·3. $C_{13}H_{11}O_2NS_2$ requires N, 5·05; S, 23·1%). The melting point of an equimolecular mixture of the two symmetrical disulphides was lowered by admixture with this substance.

Benzyl 9-anthryl disulphide was isolated from warm alcohol in yellow prisms, m. p. 128°. When it was mixed with equimolar proportions of dibenzyl and dianthryl disulphides its melting point was lowered (Found : C, 75·5; H, 4·4; S, 19·5. $C_{21}H_{16}S_2$ requires C, 75·9; H, 4·8; S, 19·3%).

Reaction of Organic Thiosulphates with Alkali Cyanide.—On

mixing aqueous solutions of potassium cyanide and the thiosulphate (equal mols.) reaction quickly ensued. It was completed by keeping the mixture for various periods, generally ½ hour, or was assisted by maintaining the temperature at about 30°. The yield of thiocyanate, which separated practically pure in most cases, was almost quantitative and a corresponding amount of sulphite was found in the aqueous liquor. In this way, the following thiocyanates were isolated.

Benzyl thiocyanate, m. p. 41° (Found: N, 9·7; S, 21·3. Calc., N, 9·4; S, 21·5%).

2-Nitrobenzyl thiocyanate, m. p. 71° (Found: N, 14·7. Calc., N, 14·4%). Cassira (*Ber.*, 1892, **25**, 3028) gives the m. p. of this substance as 75°.

4-*Nitrobenzyl thiocyanate*, colourless prisms, m. p. 79°, from warm alcohol (Found: N, 14·1; S, 16·4. $C_8H_6O_2N_2S$ requires N, 14·4; S, 16·5%).

9-*Anthryl thiocyanate*, pale yellow needles, m. p. 181°, from hot alcohol (Found: N, 6·4; S, 13·4. $C_{15}H_9NS$ requires N, 6·5; S, 13·6%).

Reaction of Di-p-toluenesulphonyl Sulphide with Mercaptans.—An alcoholic solution of the mercaptide (2 mols.) and the sulphide (1 mol.) containing 5 g. in 100—150 c.c. was warmed on the water-bath and the solvent was then evaporated, water being added towards the completion of the process. The insoluble product, in all the cases examined, was the disulphide corresponding to the mercaptan taken. The solution, containing sulphinate and thiosulphonate, was acidified and gently warmed to decompose the latter; after the addition of aqueous sodium carbonate the coagulated sulphur was collected, and the filtrate again rendered acid. The liberated sulphinic acid was in each case *p*-toluenesulphinic acid.

The disulphides obtained in this way from 2 : 5-dichlorophenyl, 6-methoxy-*m*-tolyl, and 3-chloro-6-methoxyphenyl mercaptans were identified by comparison with authentic samples from other sources.

Reaction of Sodium Tetrathionate with Mercaptides.—A typical experiment was as follows. A solution of 5 g. (2 mols.) of 6-methoxy-*m*-tolyl mercaptan in a small volume of alcohol was exactly neutralised with aqueous sodium hydroxide and added to a stirred solution of 7·5 g. (1 mol.) of sodium tetrathionate in 200 c.c. of water. The disulphide separated at once, but the mixture was kept for an hour before the solid was collected. The filtrate contained thiosulphate but no sulphite. Determinations of the iodine value were made and the roughly quantitative data obtained agreed well with the equation previously given; *e.g.* (*a*) 6-methoxy-

m-tolyl mercaptan: I value, 92%; disulphide, 97% of theory, (*b*) 3-chloro-6-methoxyphenyl mercaptan: I value, 95%; disulphide, 95%, (*c*) 2 : 5-dichlorophenyl mercaptan: I value, 98%; disulphide, 99%.

Reaction of Sodium Trithionate with Mercaptans.—The method of experiment was the same as the preceding. With benzyl, 6-methoxy-*m*-tolyl, and 2 : 5-dichlorophenyl mercaptans, the disulphides were isolated in 99—100% of the yields required by the equation previously given, whilst the approximate iodine values of the filtrates were about 90%. Estimation of the sulphite in the case of 6-methoxy-*m*-tolyl mercaptan showed 99—100% of the theoretical amount of this salt to be present in the aqueous liquor.

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King's College, London. [*Received, November 3rd,* 1925.]

CCCCI.—*Observations on the Claisen Reaction.*

By Gilbert T. Morgan and Eusebius Holmes.

Until recently the condensation of the higher methyl monoketones with esters under the influence of sodium had only been investigated up to the homologues containing the radicals *n*-hexyl and *n*-nonyl. The present investigation was undertaken to find out where, and if possible why, the reaction stopped when applied to methyl ketones containing also one of the higher alkyl radicals.

The nomenclature throughout this paper is based on the following condensation with ethyl acetate:

$$C_nH_{2n+1}\cdot CO\cdot CH_3 \longrightarrow C_nH_{2n+1}\cdot CO\cdot CH_2\cdot CO\cdot CH_3.$$

It is shown that, under the conditions stated, the reaction proceeds quite normally from $n = 7$ to $n = 19$, a satisfactory yield of 1 : 3-diketone being obtained in every case.

The general method of procedure has been to convert the corresponding fatty acid into its barium salt and to distil this with three molecular proportions of anhydrous barium acetate in a specially constructed flat vacuum pan (Morgan and Holmes, *J. Soc. Chem. Ind.*, 1925, **44**, 108T). The crude product was purified and subjected to the Claisen condensation with sodium and ethyl acetate, the sodium salt of the enolic form of the β-diketone being treated with acetic acid and the liberated diketone precipitated

and purified as its co-ordinated copper derivative. The acids $C_nH_{2n+1}\cdot CO_2H$, where $n = 10, 12, 14, 18$, were obtained by oxidising the methyl ketone from the next higher naturally occurring acid, to give acetic acid and the required acid, from which mixture the latter was isolated as its relatively insoluble barium salt.

The copper salts of the β-diketones are blue, as are the lower members of the series, but the colour becomes less pronounced as the homologous series is ascended. The diketones from $n = 7$ to 19 have been obtained as solids at the ordinary temperature, whilst the monoketones from $n = 10$ upwards are colourless solids with progressively higher melting points.

Since this work originally arose out of the researches on cyclic tellurium compounds of bactericidal potency, it is of interest to note that Mr. C. J. A. Taylor (this vol., p. 2615) has found it possible to prepare *cyclo*telluropentanedione dichlorides reducible to bactericidal *cyclo*telluropentanediones in the case of the following diketones, all of which are described in the present paper : *n*-octoylacetone, *n*-nonoylacetone and *n*-duodecoylacetone (lauroylacetone). These are the only ones so far condensed with tellurium tetrachloride, but it appears probable that the whole of the series would give similar results.

Experimental.

In the case of the lower members of the series, $n = 9$ and below, the procedure was as described below in the case of *n*-octoylacetone. For the higher members, three to nine mols. of the ester were employed, no preliminary cooling being necessary. After heating under reflux for from 4 to 5 hours, the mixture was poured on to ice as before.

The mixtures were then neutralised with acetic acid, and saturated cupric acetate was run in. In most cases, the copper salts of the diketones were precipitated at once, but for the higher ones, $n = 15$ and upwards, it was found necessary to add alcohol to bring the reagents together.

The free diketones were obtained by treating the copper salts with dilute sulphuric acid in the presence of ether, which was subsequently removed. The lower diketones were purified by vacuum distillation, the higher ones by crystallisation from alcohol.

n-*Octoylacetone*.—*n*-Heptyl methyl ketone (35 g.), obtained by the dry distillation of barium *n*-octoate with barium acetate (3 mols.), was added to ethyl acetate (2·5 mols.), the mixture cooled to 0°, and sodium (1 atom.) added in the form of thin slices. After 12 hours, the mixture was heated under reflux for 3 hours, allowed to cool, and poured on to ice. The liquid was then made very

slightly acid with dilute acetic acid, and the oily layer of liberated diketone precipitated with a saturated solution of cupric acetate. After being stirred at intervals for ½ hour, the precipitate was collected and washed with a little water and cold alcohol. A yield of 26 g. represented 47·8%. Two subsequent batches gave yields of 41·0 and 48·6%, respectively.

Crystallised successively from alcohol and benzene, the *copper* salt was obtained in pale blue needles and melted at 118°.

The salt (0·5 g.) was shaken with a few c.c. of dilute sulphuric acid in the presence of a little ether. The acid layer was separated, and a water washing of the ether layer added. The copper was precipitated by means of caustic potash, and weighed as the oxide (Found: Cu, 14·6; C, 61·6; H, 8·85. $C_{22}H_{38}O_4Cu$ requires Cu, 14·8; C, 61·45; H, 8·8%).

The *n*-octoylacetone recovered from the copper salt had the characteristic odour of the β-diketones of this series, and boiled at 248°/755 mm. and 118°/5 mm.

n-*Nonoylacetone*.—A quantity of the corresponding ketone from a reputed pure specimen of barium pelargonate (23 g.) was added to 37 g. of pure dry ethyl acetate, and 3·8 g. of sodium were added to the cooled mixture. The *copper* salt of a diketone was obtained by the general method and weighed 26·3 g., a yield of 68·8%. Recrystallised from benzene, it melted at 107°, and was of the expected pale blue colour (Found: Cu, 13·9. $C_{24}H_{42}O_4Cu$ requires Cu, 13·9%).

Since the above melting point was not in accord with those of the other members of the series, and, furthermore, other discrepancies arose when the diketone was condensed with tellurium tetrachloride, another specimen of pelargonic acid was obtained and the reactions were repeated. Again the copper salt of a diketone was obtained, purified, and analysed (Found: Cu, 13·75; C, 63·05; H, 9·4. Theory requires Cu, 13·9; C, 62·9; H, 9·2%).

This specimen melted at 115·5°, a value bringing it in line with its homologues. It appears probable that the earlier specimen of acid contained an acid isomeric with pelargonic acid but having a branched chain remote from the carboxyl group.

The *n*-nonoylacetone recovered from the copper salt boiled at 150°/15 mm.

n-*Decoylacetone*.—This diketone has been described (Morgan and Holmes, J., 1924, **125**, 760; *J. Pharm. Soc.*, June 14, 1924).

n-*Undecoylacetone*.—*n*-Decyl methyl ketone, obtained from the corresponding undecoic acid, which was itself prepared by the ketone and acidified dichromate degradation of lauric acid, was condensed with sodium and ethyl acetate (6 mols.). The

yield of *copper* salt was 3·9 g. (70%). After crystallisation from benzene the salt melted at 112° (Found: Cu, 12·4; C, 65·6; H, 10·0. $C_{28}H_{50}O_4Cu$ requires Cu, 12·4; C, 65·4; H, 9·7%).

The free diketone was obtained as a colourless solid melting at 28°.

n-*Duodecoylacetone* (*Lauroylacetone*).—Three separate batches of the monoketone obtained from lauric acid were condensed with 3, 6, and 9 molecular proportions of ethyl acetate, respectively, the period of refluxing being extended to 4 hours. The yields of *copper diketone* from 5 g. of ketone were 2·6 g., 3·45 g. (50·2%), and 3·40 g., respectively. It appears that the optimum yield of rather more than 50% was reached by using 6—8 molecular proportions of ester in the condensation. The pure salt melted at 112·5° (Found: Cu, 11·7; C, 66·6; H, 10·3. $C_{30}H_{54}O_4Cu$ requires Cu, 11·7; C, 66·5; H, 10·0%).

The free diketone was a colourless solid of melting point 31—32°.

n-*Tridecoylacetone*.—Myristic acid was converted into the barium salt and dry-distilled with barium acetate. The resulting methyl ketone was then oxidised with acid sodium dichromate to give the next lower acid, which, on subsequent distillation of its barium salt, gave the duodecyl methyl ketone. This (5 g.) was condensed with ester to give 3·7 g. of the *copper diketone*, a yield of 54%. The pure salt melted at 111° (Found: Cu, 11·2. $C_{32}H_{58}O_4Cu$ requires Cu, 11·2%).

The pure *diketone* obtained from the copper derivative was a colourless solid melting at 35°. It had scarcely any odour and gave the red ferric coloration with alcoholic ferric chloride only on warming (Found: C, 75·4; H, 11·7. $C_{16}H_{30}O_2$ requires C, 75·6; H, 11·8%).

n-*Tetradecoylacetone* (*Myristoylacetone*).—Five g. of the ketone obtained from myristic acid were subjected to the Claisen reaction, giving 3·42 g. of *copper* salt (yield 52%) which, after crystallisation from alcohol and from benzene, melted at 112° (Found: Cu, 10·5. $C_{34}H_{62}O_4Cu$ requires Cu, 10·6%).

The free *diketone* melted at 39° (Found: C, 76·1; H, 12·3. $C_{17}H_{32}O_2$ requires C, 76·1; H, 11·9%).

n-*Pentadecoylacetone*.—*n*-Tetradecyl methyl ketone was prepared from palmitic acid by the general degradation process. Condensed with ethyl acetate, it gave 2·25 g. of the *copper diketone*, a yield of 35%. The purified salt melted at 111° (Found: Cu, 10·5. $C_{36}H_{66}O_4Cu$ requires Cu, 10·2%).

The colourless *diketone* melted at 42° (Found: C, 76·4; H, 12·0. $C_{18}H_{34}O_2$ requires C, 76·6; H, 12·1%).

n-*Hexadecoylacetone* (*Palmitoylacetone*).—*n*-Pentadecyl methyl

ketone (5 g.) obtained from palmitic acid was condensed with ethyl acetate (7 mols.) by the general method, the time of refluxing being raised to 5 hours. The copper salt (yield 2·2 g.; 34%) after purification melted at 112° (Found: Cu, 9·6. $C_{38}H_{70}O_4Cu$ requires Cu, 9·7%).

The decomposition of the copper salt by dilute sulphuric acid in presence of ether took an excessive time. Accordingly, in this case and in the case of all the higher members of the series, the copper derivative was suspended in water, an equal volume of concentrated acid added, and the mixture allowed to cool before being extracted with ether.

The free *diketone* crystallised from alcohol in colourless plates, m. p. 49° (Found: C, 76·8; H, 12·3. $C_{19}H_{36}O_2$ requires C, 77·0; H, 12·2%).

n-*Heptadecoylacetone* (*Margaroylacetone*).—The condensation of the ketone (5 g.) obtained from margaric acid was carried out with 3, 6, and 9 mols. of ester, respectively, the time of refluxing being 5 hours. The yields of *copper* salt were 0·35 g., 1·7 g. (27%), and 1·4 g., and of recovered ketone, 4·0 g., 2·5 g., and 2·9 g., respectively. In each case, a small amount of copper margarate was produced. The copper salt of the diketone was washed with cold ether. The unchanged ketone was then separated from the copper margarate in the washings by acidification, treatment with barium acetate, and filtration of the insoluble barium salt.

The pure copper salt melted at 112° (Found: Cu, 9·3. $C_{40}H_{74}O_4Cu$ requires Cu, 9·3%), and the free *diketone* at 51° (Found: C, 77·3; H, 12·3. $C_{20}H_{38}O_2$ requires C, 77·4; H, 12·3%).

n-*Octadecoylacetone* (*Stearoylacetone*).—In a repetition of previous work, 10 g. of *n*-heptadecyl methyl ketone were condensed with ethyl acetate (35 mols.) and sodium, and 0·75 g. of *copper diketone* was obtained on adding cupric acetate and alcohol to the reaction mixture (yield 6%). With 8 mols. of ester, 6·9 g. of copper salt were obtained (yield 55%). No diketone copper salt was ever obtained until alcohol was added to the reaction mixture, this accounting for some of the earlier negative results. The purified salt melted at 113° (Found: Cu, 9·0. $C_{42}H_{78}O_4Cu$ requires Cu, 9·0%).

The free *diketone* crystallised from alcohol in colourless plates, m. p. 52·5°, and gave a red coloration with alcoholic ferric chloride on warming (Found: C, 77·5; H, 12·4. $C_{21}H_{40}O_2$ requires C, 77·8; H, 12·35%).

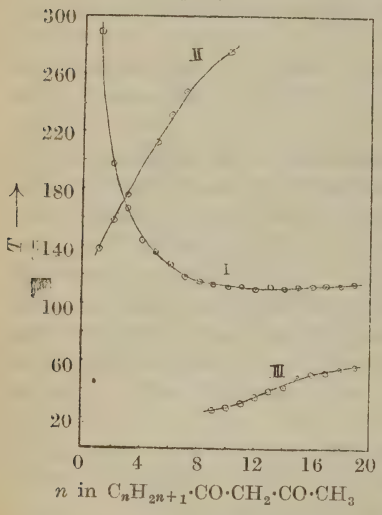
n-*Nonadecoylacetone*.—*n*-Octadecyl methyl ketone was obtained from the C_{20} acid by the general degradation process. Condensing with ethyl acetate gave a 32% yield of a *copper diketone*, some

unchanged ketone being recovered. The pure salt, crystallised from benzene, melted at 112·5° (Found : Cu, 8·6. $C_{44}H_{82}O_4Cu$ requires Cu, 8·6%).

The recovered *diketone* consisted of thin plates, m. p. 55° (Found : C, 77·9; H, 12·5. $C_{22}H_{42}O_2$ requires C, 78·1; H, 12·4%).

n-Eicosanoylacetone.—Potassium erucate was fused with caustic potash, giving acetic acid and the normal C_{20} acid, eicosanic acid. After purification, this was converted into its barium salt, which was then distilled with barium acetate. The *n*-nonadecyl methyl ketone obtained was condensed with ethyl acetate in the general manner to give the corresponding *copper* derivative, 5 g. yielding 1·75 g. (28·4%). Crystallised from benzene, the salt melted at 114° (Found : Cu, 8·15. $C_{46}H_{86}O_4Cu$ requires Cu, 8·3%).

Fig. 1.



The free *diketone* melted at 57° (Found : C, 78·4; H, 12·6. $C_{23}H_{44}O_2$ requires C, 78·4; H, 12·5%).

In the diagram, curve I shows a noteworthy change in the fusibility of copper β-diketones with lengthening of the carbon chain. Curves II and III indicate the boiling points of the lower diketones and the melting points of the higher diketones, respectively.

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University of Birmingham,
Edgbaston. [*Received, November 4th,* 1925.]

CCCCII.—*The Relation of Homogeneous to Catalysed Reactions. The Catalytic Decomposition of Hydrogen Iodide on the Surface of Platinum.*

By Cyril Norman Hinshelwood and Robert Emmett Burk.

The results of several previous investigations (this vol., pp. 327, 1105, 1552; *Proc. Roy. Soc.*, 1925, *A*, **108**, 211) have rendered

probable the conclusion that simple gaseous decompositions, which as homogeneous reactions are bimolecular, become unimolecular when they take place in contact with the surface of a solid catalyst. Thus, for example, the thermal decomposition of nitrous oxide, $2N_2O = 2N_2 + O_2$, as an uncatalysed reaction depends upon the collision of two molecules, but the reaction which takes place upon the surface of gold appears to be simply $N_2O = N_2 + O$, followed by the combination of atomic oxygen to the molecular form. The decompositions of nitrous oxide on the surface of platinum, and of ammonia on the surface of platinum have also been shown to be unimolecular.

It is not always possible to decide from measurements of reaction rate whether a catalytic reaction is unimolecular or bimolecular. If the active surface of the catalyst is completely covered with adsorbed molecules—'saturated'—then the reaction rate is independent of the pressure of the gas. The reaction appears to be of 'zero order.' When, on the other hand, the adsorption is small, the chance of a group of n molecules occupying positions on the surface near enough for interaction to be possible is proportional to the nth power of the total number adsorbed, and this in turn to the nth power of the pressure of the gas. The 'order' of the reaction obtained from kinetic measurements gives under these conditions the number of molecules actually participating in the decomposition. An intermediate condition is possible, when the adsorption is neither very large nor quite small, where a bimolecular reaction might simulate a unimolecular reaction over a small range of pressure. But if the reaction order appeared to be unity by a coincidence of this kind, it would vary very markedly both with pressure and with temperature, as may easily be seen. This state of affairs would readily be detected, and the results discounted, so that in general we may say that unless the reaction order is zero it gives the number of molecules participating in the change.

The decomposition of ammonia on tungsten, and of hydrogen iodide on gold are both approximately of order zero; consequently we cannot conclude how many molecules are involved. The homogeneous decomposition of hydrogen iodide is one of the best known bimolecular reactions. We were anxious therefore to find a catalyst at the surface of which the true order of the heterogeneous reaction could be found. Platinum fulfils these conditions. The reaction takes place in the simple unimolecular manner, $HI = H + I$, followed by the combination of atomic hydrogen and iodine to form molecules.

This illustrates once more the fundamental importance in hetero-

geneous catalysis of the affinity which metal surfaces possess for free atoms.

Method of Experiment.—The hydrogen iodide was prepared by the action of phosphoric acid on potassium iodide and purified by fractional distillation from liquid air, the middle fraction being collected in evacuated blackened glass holders.

The decomposition was allowed to take place at the surface of a heated platinum wire and measured exactly as described for the corresponding experiments with a gold wire (this vol., p. 1552). The reaction vessel was kept in ice. Since the iodine condensed, the reaction $2HI = H_2 + I_2$ is attended by a decrease in pressure which allows the rate to be measured by simple manometric means.

That the action of the platinum wire was 'catalytic,' and that the wire was not attacked by the iodine was shown by the fact that the theoretical change in pressure was observed after complete decomposition, and by the fact that the resistance of the wire remained absolutely unchanged during the whole series of experiments. Its catalytic activity, moreover, remained steady. The mercury in the manometer was protected from the action of the hydrogen iodide by a buffer of hydrogen in the capillary tube leading to the decomposition bulb.

Influence of the Pressure of the Hydrogen Iodide.—Three typical experiments showing the course of the reaction at different temperatures will first be recorded: t is the time in seconds, x the percentage change, and k the unimolecular velocity coefficient.

670°. 200 Mm. HI. 100 Mm. H_2.			563°. 200 Mm. HI. 100 Mm. H_2.			439°. 200 Mm. HI. 100 Mm. H_2.		
t.	x.	$k \times 10^4$.	t.	x.	$k \times 10^4$.	t.	x.	$k \times 10^4$
100	22	24·9	120	12	10·6	600	13	2·32
200	41	26·4	300	27	10·3	1200	26	2·50
300	56	27·4	600	47	10·6	1800	38	2·65
400	64	25·6	900	61	10·5	2400	45	2·49
500	72	25·5	1200	71	10·4	3300	55	2·42
600	76	24·0	1500	78	10·1	4200	63·5	2·40
						6000	74·5	2·28

The influence of the pressure of the hydrogen iodide is shown by the following values found at 563°. 100 Mm. of hydrogen were present in each experiment.

Press. of HI (mm.)	100	200	300
k	0·00118	0·00105	0·00095

The values of k are sufficiently independent of pressure to show that the reaction is unimolecular. The slight dropping off was traced to the circumstance that hydrogen has a small but definite retarding effect on the reaction. When the initial pressure of

hydrogen iodide is great, the pressure of hydrogen at every stage of the reaction is greater than when the initial pressure of hydrogen iodide is small. The slight falling off in rate due to the adsorption of hydrogen by the wire is shown by the following table. 200 Mm. of hydrogen iodide were used in each experiment.

Press. of H_2 (mm.)	0	100	200
k (average)	0·00126	0·00105	0·00092

The Influence of Temperature.—This is shown in the following table. The values of k are those corresponding to a hydrogen pressure of 100 mm.

T (abs.)	943°	836°	712°
k	0·00268	0·00105	0·000244
E (cals.)		13,700	13,850

Mechanism of the Reaction.—We suggest the simplest possible interpretation of the results, namely, that the reaction at the surface of the platinum is the simple change $HI = H + I$. The apparently unimolecular course could be explained in another way by assuming that there existed one complete layer of hydrogen iodide molecules on the surface of the catalyst and that reaction took place when a molecule from the gas phase struck one of the molecules in this layer. There are, however, several vital objections to this. First, there is abundant evidence to show that where two molecules interact in heterogeneous reactions they must in general both be actually adsorbed. This is shown by the fact that in reactions where A and B interact excess of either A or B can actually retard the reaction by displacing the other from the surface. Secondly, if there is a complete layer there is no reason why the molecules in it should not react among themselves instead of waiting for impacts from the gas phase. Thirdly, if the heterogeneous reaction depended upon impacts from the gas phase, the rate could never become independent of pressure as it does when it takes place at the surface of gold.

Attention may be directed to one further point of interest which emerges from these experiments. The retarding effect of hydrogen on the reaction is but slight. When the catalytic decomposition of ammonia was investigated on the same wire—and actually at a higher temperature—it was found to be retarded in a most pronounced manner by hydrogen. It cannot be argued that hydrogen iodide is too strongly adsorbed to be displaced by hydrogen whilst ammonia is easily displaceable, because the course of a unimolecular reaction can be revealed only when the adsorption is small. Hence we must conclude once more that different reactions are provoked at different points (' active centres ') on the catalytic surface.

Summary.

In continuation of a general investigation of the influence of catalytic surfaces on reactions which in the homogeneous gas phase are bimolecular, it has been shown that the thermal decomposition of hydrogen iodide in contact with platinum is kinetically unimolecular. Reasons are given for believing that this proves the decomposition to take place in the simple manner $HI = H + I$.

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CCCCIII.—*Oxidation of Ethyl Ether to Oxalic Acid in Presence of Uranyl Nitrate.*

By SYDNEY WILLIAM ROWELL and ALEXANDER SMITH RUSSELL.

WHEN uranyl nitrate dissolved in ether is exposed to sunlight in presence of water a yellow precipitate sometimes forms in the aqueous layer, especially after the solution has been standing in the light for some days; at other times, a black, slimy mass forms in the aqueous layer. These compounds are the subject of the present investigation. There is only one reference in the literature to the composition of the yellow compound (Soddy, "Chemistry of the Radioelements," 1911, p. 32). Soddy found that a yellow powder of empirical formula UCH_4O_6 remained after distilling the ether from an ethereal solution of uranyl nitrate. On decomposition, this compound formed a basic carbonate which lost carbon dioxide and water at 200—300°.

EXPERIMENTAL.

Preparation of the Yellow Compound.—In a typical experiment, a mixture of 60 g. of ethyl ether, 60 g. of uranyl nitrate and 20—60 g. of water, after being shaken until the nitrate dissolved, was exposed to bright sunlight for periods up to 24 hours. The ether was then removed by distillation at as low a temperature as possible, and the aqueous solution evaporated. On cooling, there separated a yellow compound mixed with uranyl nitrate which was freed from the latter by washing with cold water, in which the former was comparatively insoluble. The yield was poor and rarely exceeded 12 g. The yellow compound was found to be identical in properties with the normal hydrated oxalate of uranium, $UO_2C_2O_4,2H_2O$ (Found: U, 60·5; C_2O_4, 22·2; H_2O, 9·7; C, 6·1; H, 1·2. Calc., U, 60·4; C_2O_4, 22·3; H_2O, 9·1; C, 6·1; H, 1·0%).

Uranium was determined gravimetrically as U_3O_8, and oxalate volumetrically.

Formation of a New Basic Oxalate of Uranium.—In a few of the above experiments the compound which resulted appeared different from the normal oxalate; it had a lighter yellow colour. It gave the usual reactions of an oxalate (Found: U, 68·0; C_2O_4, 12·0%). The basic oxalates which correspond with the normal oxalates would be $U(OH)_4,UO_2C_2O_4,2H_2O$ and $UO_2(OH)_2,UO_2C_2O_4,2H_2O$, depending whether the uranium in the hydroxide is quadri- or sexa-valent. The former of these contains U, 68·0; C_2O_4, 12·6% and the latter U, 68·2; C_2O_4, 12·6%. Either of these might be the compound analysed above. Since the compound $U(OH)_4$ is stabler than $UO_2(OH)_2$, we are inclined to prefer the first formula. It may be written UCH_4O_6, which is identical with that of Soddy's product. The formula of the other product, so written, differs, however, only by a single hydrogen atom. There is no doubt that a basic oxalate is formed by the interaction of uranyl nitrate and ether in the presence of sunlight and it is probable that Soddy's product was this oxalate.

Formation of Uranous Hydroxide.—We find that when uranyl nitrate in solution in ether is neutralised so that a precipitate is just not formed and exposed to sunlight for periods of a few hours, there settles from solution a black or greenish-black, slimy precipitate which accompanies the basic and normal oxalates. It is not formed in solutions of uranyl nitrate containing free nitric acid. It resembles the product obtained by adding ammonia to a solution of a uranous salt, namely $U(OH)_4$, and this composition was confirmed by analysis (Found: U, 78·0. Calc., U, 77·8%). These observations are in agreement with the work of Aloy and Rodier (*Bull. Soc. chim.*, 1920, **27**, 101; 1922, **31**, 246), and of Aloy and Valdiguié (*ibid.*, 1925, **37**, 1135), who found that in neutral solution uranium salts on exposure to sunlight in the presence of certain organic compounds yield a black or a violet precipitate, the former being uranous hydroxide and the latter of composition $U_3O_8,2H_2O$, through partial reduction of the uranyl salt. It is evident from these results that the composition of these lower oxides, like that of the oxalates, varies with the conditions in which they are formed.

Suggested Mechanism of the Reaction.—In the absence of sunlight, none of the products described above is formed. Exposure to sunlight is therefore essential to the reactions. The oxalates formed are not oxidation products of an impurity in the ether, for the most carefully purified ether gave the oxalate, and addition of alcohol, the most likely impurity, did not increase the yield. Moreover, no oxalate resulted when alcohol replaced ether in the solution

of uranyl nitrate, although we found, as Aloy and his co-workers did, that it favours the formation of a hydroxide of uranium in neutral solution. No oxalate was obtained when other uranyl salts replaced the nitrate. Ebelman (*Ann. Chim. Phys.*, 1842, **5**, 198) first pointed out that solutions of the uranyl salts of strong acids were changed by sunlight in presence of an oxidisable compound, acquiring a green colour which we now know to be due to uranous salts, and this work has been greatly extended by Aloy and co-workers (*loc. cit.*). On their view, if A be an acceptor of oxygen, *e.g.*, alcohol, and uranyl nitrate the salt considered, the reaction proceeds in sunlight as $UO_2(NO_3)_2 + 2HNO_3 + A = U(NO_3)_4 + H_2O + AO$ in presence of a sufficiency of nitric acid. If sufficient acid be not present, it is to be expected that some uranous hydroxide would be formed, and this is what we have found. When ether is the acceptor, it is oxidised finally, we find, to oxalic acid. In presence of uranyl ion and free nitric acid, this would be expected to form the normal oxalate as it does; in presence of insufficient acid, a mixture of the normal oxalate and uranous hydroxide or a compound of these would be expected to form. We find the latter.

The manner of oxidation of ether to oxalic acid has not been previously considered in the literature. We suggest the following. Ether is oxidised to diglycol when the uranyl is reduced to the uranous ion by sunlight. Part of the diglycol is oxidised by nitric acid to diglycollic acid and part hydrolysed to glycol, which is then further oxidised by nitric acid to oxalic acid, thus :

$$\text{Ether} \longrightarrow \text{diglycol} \begin{cases} \nearrow \text{diglycollic acid.} \\ \searrow \text{glycol} \longrightarrow \text{oxalic acid.} \end{cases}$$

It is, of course, known that diglycol is oxidised by nitric acid partly to oxalic acid but mostly to diglycollic acid. It has not yet been possible to test this scheme by showing the presence of either diglycol or diglycollic acid.

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Christ Church, Oxford. [*Received, November 23rd,* 1925.]

CCCCIV.—*Polymerisation of β-Glucosan. The Constitution of Synthetic Dextrins.*

By James Colquhoun Irvine and John Walter Hyde Oldham.

One method of approach to the constitutional problems of the polysaccharides is through the study of anhydro-hexoses, and the discovery by Pictet and his collaborators that β-glucosan can be prepared conveniently by the dry distillation of starch acquires a special importance in this connexion. 1 : 6-Anhydroglucose has in this way been rendered available in quantity and its properties have been examined in detail by Pictet and others. One of the most striking of the new observations is that the compound is readily polymerised, the reaction $n(C_6H_{10}O_5) \longrightarrow (C_6H_{10}O_5)_n$ proceeding readily when β-glucosan is heated, either alone or in the presence of catalysts. Thus, when fused with platinum black, glucosan is converted into an amorphous powder, to which the formula $(C_6H_{10}O_5)_4$ applies, and this displays the general properties of a dextrin, yielding glucose on hydrolysis (Pictet, *Helv. Chim. Acta*, 1918, **1**, 226). Pictet, finding platinum black uncertain in its action, improved the method by using zinc chloride as a catalyst (*ibid.*, 1921, **4**, 788) and he also varied the procedure by conducting the polymerisation under both reduced and increased pressure. Four definite compounds were obtained under these conditions :

	Polymeride.	$[\alpha]_D$.	Pressure.
1.	Diglucosan	+ 28·2°	15 mm.
2.	Tetraglucosan	+111·9°	1 atmos.
3.	Hexaglucosan	+ 94·1°	4·6 ,,
4.	Octaglucosan	+ 72·8°	13·2 ,,

Although there seems no theoretical limit to the number or variety of possible polymerides, the above list includes only compounds in which glucosan molecules may be regarded as having become associated in multiples of two. The mode of attachment of the parent molecules has hitherto, save in one case, remained obscure, but Pictet has recorded the abnormality that the polymerides yield only diacetates or dibenzoates in place of the tri-derivatives to be expected.

By arrangement with Professor Pictet, we have been engaged on the constitutional study of the polyglucosans and take this opportunity of expressing our thanks for his courteous permission to extend his work. The completion of the investigation, which was commenced four years ago, has been delayed in consequence of the complexity of the results, and, in the meantime, Pringsheim

has described the application of the methylation process to tetraglucosan (*Ber.*, 1922, **55**, 3001). No difficulty was apparently experienced by him in obtaining complete alkylation and, on hydrolysis of the product, both tetramethyl and dimethyl glucose were obtained. This is a striking result, but, as shown by Pringsheim, it is in itself insufficient to discriminate between two alternative structures for tetraglucosan.

In order to obtain an adequate view of the mechanism of the polymerisation of glucosan, it is necessary to study the constitution of a variety of polymerides displaying a progressive increase in molecular complexity, and this we have accomplished. In repeating Pictet's experiments little success was attained in using platinum black as a catalyst and, after numerous attempts to find a superior reagent, we adopted the method of heating glucosan at 250° in the presence of zinc dust. The polymerisation was conducted in a vacuum, the residual air having been washed out with hydrogen and, under these conditions, the change took place without charring or alteration in weight.* As the zinc dust employed contained a trace of chloride, it is possible that the latter is the functional catalyst, as we find that zinc chloride exercises a powerful polymerising effect on glucosan and its derivatives, the reaction in some instances being violent. For many reasons we prefer the use of metallic zinc, and, although polymerides differing from those described by Pictet are produced, we have continued to employ the process, as it proved satisfactory for large-scale working and gave uniform results. It may be remarked, however, that the relative yield of the different dextrins is affected, not only by the catalyst, but also by the temperature, by the duration of heating, and by the scale of working.

In order to obtain polymerides of high molecular weight, it is unnecessary in our experience to work under positive pressures, and all our preparations were carried out at 15 mm. By means of fractional precipitation from aqueous solution the polymerides were separated into three main fractions, which, in order of increasing solubility, showed the following progressive diminution in

* It may be mentioned that glucosan is much less stable at high temperatures, particularly in the presence of acids, than the method of preparing the compound would suggest. Nevertheless Venn (*J. Text. Ind.*, 1924, **15**T, 414), having found that the yield of glucosan from cellulose is greatest when the acidity of the distillate is lowest, states that this result is opposed to our views as to the origin of the hexosan. It would have been surprising if any other result had been obtained and Venn's observation, which amounts to no more than the statement that the best yields of glucosan are obtained under the most favourable experimental conditions, has no bearing on the mechanism of the reactions in which glucosan is formed.

specific rotation. Dextrin I + 83·9°; Dextrin II + 60·7°; Dextrin III + 29·9°. In marked distinction to the products described by Pictet, all the dextrins yielded a definite triacetate, and the presence of three hydroxyl groups per C_6 unit was confirmed by methylation. The convenient solubilities of these trimethyl dextrins rendered possible the determination of their molecular weights in benzene solution and, in this way, the parent compounds were characterised as containing respectively seven, four, and three glucosan units.

Methylated product.	Mol. wt. (found).	Mol. wt. (calc.).	Parent compound.
Trimethyl Dextrin I	1446	1428	Heptaglucosan
,, ,, II	874	816	Tetraglucosan
,, ,, III	595	612	Triglucosan

This does not exhaust the list of polyglucosans, as we have also obtained other isomerides, and it is evident that both odd and even numbers of glucosan molecules are capable of forming polymerides. Further, it is clear that the tetraglucosan examined in the course of the present investigation is different from that described by Pictet and subsequently examined by Pringsheim. The distinction is shown in the specific rotations of the compounds, in the m. p. of the triacetates prepared from them and, most emphatically, in the different behaviour of their methylated derivatives on hydrolysis.

The methylated dextrins, which may now be termed hepta-, tetra-, and tri- (trimethyl glucosan), respectively, were examined so as to give an insight into the mode of attachment of the constituent hexose chains, the information being derived by identifying the methylated glucoses formed on hydrolysing each compound. In order to indicate the significance of these results, it may be recalled that, although it is customary to distribute the hydroxyl groups equally among the C_6 units of a polysaccharide or allied compound, this allocation is based on an assumption and should be subjected to experimental test in each case. Thus, cellulose and hexa-amylose (Irvine, Pringsheim, and Macdonald, J., 1924, **125**, 942), which are isomeric with the dextrins now under consideration, give trimethyl derivatives and these, in turn, yield on hydrolysis 2 : 3 : 6-trimethyl glucose and no other sugar. It follows that the hydroxyl groups in the parent compounds are uniformly distributed, *i.e.*, each C_6 unit carries three hydroxyls arranged in the same positions. Were this not the case, isomeric trimethyl glucoses would be formed or, alternatively, a mixture of methylated sugars, such as tetramethyl and dimethyl glucoses, giving the same average composition.

In marked contrast to natural polysaccharides, the synthetic

dextrins afford striking examples of compounds constituted on an entirely different model in that the hydroxyl groups are not attached uniformly to the individual C_6 units. We have already shown (J., 1921, **119**, 1744) that when β-glucosan is subjected to consecutive methylation and hydrolysis it gives 2 : 3 : 5-trimethyl glucose and, on the basis of analogy, it might reasonably be expected that the same end-product would be obtained from a polymerised glucosan. Such is not the case. Each trimethyl dextrin was converted into the corresponding methylated methylglucosides and thereafter into the constituent sugars, but the product, in place of being homogeneous, consisted in each case of di-, tri-, and tetramethyl glucose, mixed in proportions which gave the analytical figures required for a trimethyl glucose alone. The individual sugars were separated and two of them were characterised as 2 : 3 : 5 : 6-tetramethyl glucose and 2 : 3 : 5-trimethyl glucose, but the constitution of the dimethyl sugar is still uncertain and two alternatives are possible. Although in this section of our work we did not conduct the separation of the above sugars on quantitative lines, good reasons exist for the belief that hepta-, tetra-, and tri-(trimethyl glucosan) all give the same methylated glucoses, as the physical constants of each mixture were identical.

It is necessary to emphasise that the tetramethyl glucose isolated in these experiments is a genuine scission product of the methylated dextrins, and does not originate in any molecular cleavage during the methylation process. This possibility was carefully excluded, and the result in itself disposes of the idea that the polymerisation of glucosan is merely the union of intact molecules in pairs. The process is evidently complex and consists essentially in the formation of glucosidoglucosides which show a general structural resemblance with the constitutional type ascribed by Hess to cellulose. The development of structural formulæ for the polyglucosans demands, however, a knowledge of the relative proportions of the different methylated glucoses into which they can be transformed. A considerable advance was made by conducting all the operations, from the polymerisation of the glucosan to the separation of the methylated glucoses finally obtained, on strictly quantitative lines. For this purpose large quantities of material were required and a substantial simplification was effected by methylating the total polymerised product and separating the isomerides by vacuum distillation, without isolation of the parent compounds. The first fraction consisted of monomeric trimethyl glucosan, whilst the second was a viscous syrup which was shown to be di (trimethyl glucosan). The remaining syrup, which constituted the largest fraction, was practically non-volatile at 200°/0·4

mm. and, on cooling, it solidified to a clear red glass. As this product contained all polymerides higher than the dimeride, it is termed poly (trimethyl glucosan).

Di(trimethyl glucosan) was converted into the methylglucosides of the constituent sugars, the products being formed in the proportions shown below :

		Yield %. Found.	Yield %. Calc. for equal mols.
Di(trimethyl glucosan) →	Dimethyl methylglucoside.	46·6	47·1
	Tetramethyl methylglucoside.	53·4	52·9

These proportions were confirmed from the yields of the corresponding sugars when, as before, 2 : 3 : 5 : 6-tetramethyl glucose was isolated together with a dimethyl glucose.

An equally significant result was obtained by similar treatment of poly(trimethyl glucosan), three glucosidic products being obtained in place of two.

		Yield %. Found.	Yield %. Calc. for equal mols.
Poly(trimethyl glucosan) →	2 : 3 : 5 : 6-Tetramethyl methylglucoside.	35·5	35·3
	2 : 3 : 5-Trimethyl methylglucoside.	33·5	33·3
	Dimethyl methylglucoside.	26·0	31·4
	Monomethyl methylglucoside.	5·0	

As shown by the analytical figures quoted in the experimental part, the small amount of monomethyl methylglucoside is attributable to incomplete methylation and may be added to the yield of the higher homologue.

Discussion is simplified by tabulating the significant facts showing the mutual relationships between glucosan and the polymerides now described.

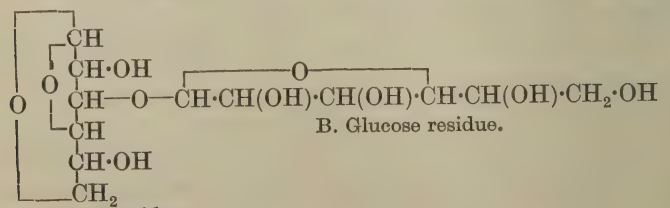
	$[\alpha]_D$ of parent compound. (water)	$[\alpha]_D$ of trimethyl derivative. (MeOH)	Mol. wt. of trimethyl derivative.	% Methoxyl content of derived glucosides.	Methylated sugars produced.
3-Glucosan ...	−65·4°	−53·2°	212 (204)	50·9	2 : 3 : 5-Trimethyl glucose.
Diglucosan ...	—	+48·3	418 (408)	51·2	2 : 3 : 5 : 6-Tetramethyl glucose. Dimethyl glucose.
Triglucosan ...	+29·9	+52·8	595 (612)	49·7	2 : 3 : 5 : 6-Tetramethyl glucose. 2 : 3 : 5-Trimethyl glucose. Dimethyl glucose.
Tetraglucosan	+60·7	+68·7	873 (816)	49·6	" "
Heptaglucosan	+85·8	+89·4	1446 (1428)	50·4	" "
Polyglucosan	—	—	—	50·6	The above tetra-, tri-, and dimethyl glucoses in exactly molecular proportions.

Including Pictet's results, a series of polymerides from mono- to octa-glucosan is now complete with the exception of the penta-form. It will be observed from the table that polymerisation alters the sign of rotation, which increases, in the dextro sense, with the molecular magnitude, this possibility having been fore-

seen through our studies of inulin and starch. The optical effect of methylation is also consistent with previous experience, but the essential fact which emerges from the results given in the table is that mono- and di-glucosan are unique members of the series. The former gives rise to only one methylated sugar (2 : 3 : 5-trimethyl glucose) and the latter yields a mixture from which trimethyl glucose is absent. Thereafter, in the higher polymerides, 2 : 3 : 5-trimethyl glucose is again encountered as an end-product and, in the case of the mixed polyglucosans, this sugar is present in equimolecular proportion with the higher and lower homologues. This represents an average result, to which all polymerides higher than diglucosan have contributed, and the discussion can therefore be focussed on the three types represented by (*a*) mono-, (*b*) di-, and (*c*) poly-glucosan.

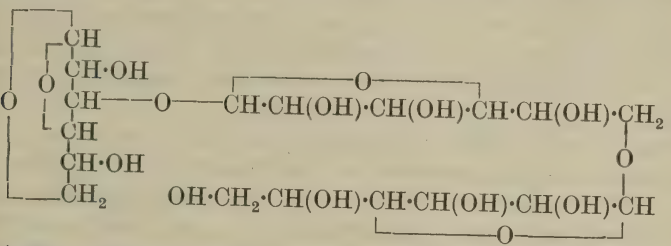
Mechanism of the Polymerisation.

The initial step of the polymerisation can be traced from the significant fact that 2 : 3 : 5 : 6-tetramethyl glucose and a dimethyl glucose are invariable products from all the polyglucosans. It follows that the first action is the conversion of glucosan into glucose, one molecule of which condenses with a second molecule of glucosan so that, once the process is initiated, it is catalytically continued. The experimental conditions employed in the polymerisation are favourable to this cycle of reactions, and no other explanation seems possible. If this be correct, the dimeride should differ from the monomeric parent in having the hydroxyl groups unequally distributed in the ratio of four in one glucose residue to two in the other. The results obtained show that this consideration applies quantitatively. The precise way in which glucose condenses with a molecule of glucosan must nevertheless remain unknown until the constitution of the dimethyl glucose isolated from diglucosan has been established, and, despite laborious investigation, this has not been solved. As shown in the experimental part, however, the sugar must be either 2 : 3- or 2 : 5-dimethyl glucose and, as the latter alternative is more strongly supported, it is provisionally adopted, leading to the following structure for diglucosan:



A. Glucosan residue. B. Glucose residue.

Speculation on the next stage of the polymerisation is guided by the fact that all polymerides above diglucosan give 2 : 3 : 5-trimethyl glucose. This can originate only from the molecular fragment B and not from A as, otherwise, the methylated sugars obtained from triglucosan would be two molecules of tetramethyl glucose and one molecule of monomethyl glucose. The attachment of the third glucose residue is thus definitely restricted to position 6 of residue B, giving the following constitution for triglucosan :



As the yields of methylated sugars from tetra- and hepta-glucosan have no quantitative significance, it is inadvisable to discuss the further steps involved in the polymerisation, but the examination of the mixed polyglucosans contributed valuable information. On occasions, these higher glucosans formed as much as 75% of the total material polymerised, so that they may be regarded as representative of the whole reaction. Inspection of the experimental details will show that this material not only gives the three methylated sugars required by the above formula, but does so in precisely equimolecular proportions. This result has been verified on more than one occasion; it cannot be regarded as adventitious and it disposes of the possibility that the trimethyl glucose originates in a simple polymeride of glucosan in which the molecular constitution of the parent molecule is preserved. It is, nevertheless, conceivable that molecules of monomeric glucosan may become associated, either together or with simple polymerides, and the existence of such compounds as hepta- and octa-glucosan indicates that this should not be ruled out. Further, the tetraglucosan examined by Pringsheim yielded no trimethyl glucose, but gave rise to the same sugars as we have now shown to originate from diglucosan. Taking a general survey of the results, it is clear that the polymerisation involves reactions of two types: one involving association and the other condensation. For example, when diglucosan is formed it may either condense with an additional molecule of glucosan to give the trimeride which, in turn, by further condensation yields a tetrameride, or alternatively, two trimeride molecules may become associated to give an entirely

different type of tetraglucosan. The inclusion of Pringsheim's results with our own renders this view more than speculative and a similar complexity may accompany each stage of the polymerisation. Our results do not provide conclusive evidence on this point and reveal only the primary nature of the polymerisation. It is of special interest to note that two-thirds of the triglucosan formula consists of a residue present in the accepted formula for maltose, a remarkable similarity in structure considering the drastic conditions employed in the preparation of the trimeride. Triglucosan may, in fact, be regarded as *glucosan maltoside*. Further, the β-configuration of the parent glucosan is preserved in the higher polymerides, despite the pronounced changes in rotation which accompany their formation.

The view now put forward demands that the condensation type of polymerisation is dependent on the presence of free hydroxyl groups, and is supported by the fact that trimethyl glucosan was recovered unchanged when heated with zinc dust in an exhausted sealed tube at 250° for 10 hours. Under similar conditions the use of zinc chloride as a catalyst resulted in profound decomposition, but, on limiting the reaction to 3 hours at 160°, the rotation altered from lævo to dextro owing to conversion of the glucosan into trimethyl glucosidotrimethyl glucose.

Applicability of the Methylation Process to the Structural Problems of Carbohydrates.

The criticism has been put forward that our method of determining the structure of carbohydrates, although diagnostic in the case of simple sugars, may not be applicable to the "closed-chain structures" represented by polysaccharides and similar compounds. It is difficult, in view of the mass of consistent results obtained with many types of non-reducing carbohydrates, to find any justification for this objection; but as at present much reliance is placed on the validity of the methylation process as a means of determining constitution, the occasion is opportune to take into account the essential requirements of the method.

The principles developed in this laboratory can be applied to the structural problems of carbohydrates, provided the following primary conditions are satisfied: (1) that methylation does not alter the configuration of a sugar; (2) that methylation does not disturb the positions in which sugar residues are attached to each other, or to other groups; and (3) that, under the conditions employed in methylation and in hydrolysis, non-glucosidic methoxyl groups do not migrate from one position to another in a sugar chain. In default of direct experimental evidence to the contrary,

and in view of the following observations, it may be claimed that the above requirements are satisfied. According to circumstances, the methylation of carbohydrates, as practised by us, is effected either by the silver oxide reaction or by the methyl sulphate method, used independently or in succession. It has been adequately proved that these alternative methods, when applied to the same compounds, give the same methylated sugars, the only distinction being that the alkaline reagent acts upon reducing sugars to give a larger excess of the corresponding β-glucoside. Configuration is therefore affected, but only so far as the reducing group is concerned. The one aspect of configuration, however, which is utilised in our deductions is that of the non-reducing groups, and it has long been known that the silver oxide reaction yields derivatives which retain the configuration of the parent compound. The conversion of *d*-dimethoxysuccinic acid into *d*-tartaric acid (Purdie and Barbour, J., 1901, **79**, 972) is a convincing, but by no means unique, example of this regularity. In addition, mono-, di-, tri-, and tetra-methyl glucose, all of which were prepared by the silver oxide reaction, have been demethylated and converted into glucose phenylosazone showing the correct optical activity.

That the second and third requirements of the method are fulfilled is shown in numerous ways. For example, Haworth and Leitch subjected maltose and cellobiose to identically the same methylating treatment, yet isolated isomeric trimethyl glucoses in the two investigations. This result cannot be reconciled with the idea that molecular linkages are altered by methylation or that the methyl groups fail to retain their positions. The evidence is equally clear in the case of the more unstable types of carbohydrate derivatives such as γ-glucosides and the existence of isomeric tetramethyl glucoses and of the corresponding tetramethyl fructoses, which reflect accurately the essential properties of the compounds from which they are derived, may be quoted in illustration. In this connexion, it is important to note that with the exception of the glucosidic alkyl group (which, in any case, is not concerned with our structural studies) the stability towards acids and alkalis of the methyl groups in a sugar chain is remarkable. Concentrated sodium hydroxide at the boiling point has no effect on a fully methylated hexose and, in our experience, the elimination of the methyl groups from an alkylated reducing sugar has been accomplished only by such processes as boiling with concentrated hydriodic acid, heating under pressure with glacial acetic acid saturated with hydrogen bromide, or, in one example,* by prolonged action with

* This result, which is unpublished, was obtained with a dimethyl galactose which yielded a monomethyl galactosazone. A similar irregularity is reported

the phenylosazone reagents. This stability is far removed from that encountered in cases where methyl groups have been shown to migrate or to enter an irregular position (see Kubota and Perkin, this vol., p. 1889).

It is possible that the frequency with which 2 : 3 : 6-trimethyl glucose has been obtained from different polysaccharides may have suggested the idea that the reagents had converted definitely isomeric compounds into a common form so that the same sugar would inevitably be produced in all cases. The results of the present investigation go far to refute this remote possibility. The only practical distinction between the alkylation of a polysaccharide and that of a simple sugar is that, owing to solubility difficulties and to steric hindrance, it is necessary in the former case to use the methyl sulphate method throughout and to repeat the methylation many times. This treatment may conceivably affect the degree of polymerisation of a compound, but as the discussion does not involve this point it may be focussed on the question if the repeated use of the alkaline reagent gives results divergent from those obtained by restricted treatment with silver oxide and methyl iodide. For this purpose, we have selected β-glucosan as a test substance and, after ten methylations by means of methyl sulphate, obtained a normal yield of the same crystalline trimethyl glucosan formerly prepared by the alternative method (Irvine and Oldham, *loc. cit.*). On extending the process until a total of twenty treatments had been given, the same product was again obtained. The result shows that even when the methyl sulphate process is repeated as often as in the case of cellulose, starch, and glycogen, the methyl groups enter the same positions in glucosan as they do when the silver oxide reaction is used only once, and, further,

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by Freudenberg and Hixon (*Ber.*, 1923, **56**, 2119) and confirmed by Levene and Meyer (*J. Biol. Chem.*, 1924, **59**, i, 145), who found that a monomethyl mannosediacetone was completely hydrolysed by treatment with very dilute acid, a property which indicates that the compound was a γ-methylmannoside diacetone. Should this prove to be the case, rearrangement may have taken place between a methyl group and an *iso*propylidene group during either methylation or hydrolysis. Numerous examples are now known of the reversible displacement of *iso*propylidene and methyl, but the reaction proceeds in acid solution, whereas Freudenberg's process does not admit of this condition. Apparently the configuration of mannose is conducive to irregular results. It may be recalled (Irvine and Paterson, J., 1914, **105**, 915) that one hydroxyl group in mannitol resists methylation completely and that, when methylglucosamine (α-amino-methylmannoside) is acted upon by dilute nitrous acid, not only is the amino-group removed, but the methyl group, which is otherwise remarkably stable, also is eliminated. In consequence, the alkylated mannoses have not been applied by us to structural studies.

that alkyl groups show no tendency to migrate to the 2 : 3 : 6-positions. The dextrins described in the present paper were also subjected to repeated methylation, yet the sugar finally obtained consisted exclusively of 2 : 3 : 5-trimethyl glucose and no trace of the 2 : 3 : 6-isomeride was detected. Precisely the converse applies when cellulose is subjected to parallel treatment, as 2 : 3 : 6-trimethyl glucose alone constitutes the final product. It is difficult to imagine that these sharply differentiated results, obtained under duplicate conditions, are due to the vagaries of the reagents rather than to inherent structural differences in the parent compounds.

Clearly, however, the silver oxide reaction when applied to polymerides tends to lower the degree of polymerisation, as indicated by a change in solubility and an alteration of the rotatory power in the direction of that of the parent unit. This phenomenon has already been encountered in the investigation of methylated inulin and has again been observed when, for comparative purposes, the mixture of higher polyglucosans was subjected to this reaction.

Experimental.

Polymerisation of β-Glucosan.—As the polymerisation of β-glucosan gives rise to a variety of isomerides, it is necessary to specify accurately the experimental method adopted in preparing the polymerides now described. In the first series of preparations, small quantities (7 g.) of glucosan were used in each experiment and this weight of material, together with 0·1 g. of zinc dust, was introduced into a 300 c.c. distilling flask, the neck of which was sealed by a cork carrying a manometer. To the side limb a T-tube was attached, provided on one branch with a tap (A) leading to the water pump and, on the other, with two taps (B and C). These were placed closely together so that the enclosed volume was small, C being connected to a supply of pure dry hydrogen. The flask, which with the exception of the side fittings was immersed in an asbestos air-bath provided with windows, was exhausted, and the residual air washed out with hydrogen. After again evacuating, the temperature of the bath was raised to 250°, the tap A being closed when the glucosan began to melt, as otherwise the compound volatilised unchanged. After about 15 minutes the melt became viscous and, as frothing ensued, the tap A was opened at intervals. In approximately 30 minutes from the start of the reaction, the frothing usually became most severe and it was then necessary to close A and C, and open B momentarily. A bubble of hydrogen was thus introduced which served to break the film of glucosan, and thereafter both C and A were rapidly opened and closed. In from 60 to 75 minutes from the time the glucosan was thoroughly melted,

frothing became sluggish and, unless A remained open for a considerable time, ceased entirely. At this stage, heating was stopped and the flask allowed to cool, the vacuum being maintained. No loss of weight was recorded under the above conditions and no charring took place.

Direct Isolation of Polyglucosans.

The product of several preparations was extracted with the minimum quantity of hot water and, on the addition of rectified spirit to the united solutions, a dark-coloured precipitate was formed. This was removed and absolute alcohol added to the filtrate. The dextrin then separated as a fine powder except in cases where too much water was present, when a sticky precipitate was produced. In such an event the liquid was decanted, the residue dissolved in a small quantity of warm water and, after removal of the solvent, dried at 100°/15 mm.; the product could then be readily powdered. The less-soluble dextrin obtained as above is referred to as "Dextrin I." The mother-liquor which had deposited Dextrin I was concentrated and the addition of alcohol repeated until no further precipitate was formed. In this way the material was separated into two further portions (Dextrins II and III), each fraction being relegated to its class on the basis of solubility and specific rotation.

Examination of Dextrin I. Heptaglucosan.—The material was redissolved in hot water and boiled with charcoal, a treatment which removed colouring matter and also diminished the yield considerably. Finally, the compound was precipitated with alcohol and dried in a vacuum. *Dextrin* I was thus obtained as a slightly hygroscopic powder which, although perfectly white, gave a pale yellow solution in water. Analysis of different preparations gave C, 44·5, 44·45; H, 6·4, 6·2; ash, 0·266 ($C_6H_{10}O_5$ requires C, 44·4; H, 6·2%). Dextrin I is insoluble in organic solvents, with the exception of acetic acid, but is freely soluble in water, giving a non-reducing dextrorotatory solution. $[\alpha]_D + 83·9°$ for $c = 2·08$. This value was obtained in different preparations and when a specimen of the material was fractionally precipitated with alcohol the most active fraction showed $[\alpha]_D + 85·8°$, thus indicating the uniformity of the compound. Despite this observation and the fact that dextrin I was afterwards shown to be heptaglucosan, the application of Karrer's method of determining the molecular magnitude of polymerised units by analysis of the sodium hydroxide compounds gave inconclusive results which lay between those required for $(C_6H_{10}O_5)_3$ and $(C_6H_{10}O_5)_4$.

For analytical and reference purposes the *triacetate* was prepared

by boiling the dextrin, until dissolved, with excess of acetic anhydride containing zinc chloride. The product was isolated by precipitation with water, washing with ether and solution in a large excess of hot absolute alcohol, from which it separated as a fine, white powder. After three such treatments, the m. p. was constant (142°) (Found : C, 49·95; H, 5·6; $CH_3 \cdot CO_2H$, 65·6. $C_{12}H_{16}O_8$ requires C, 50·0; H, 5·55; $CH_3 \cdot CO_2H$, 62·5%). The triacetate is insoluble in water, cold absolute alcohol, or ether, soluble in other organic solvents including aqueous alcohol. $[\alpha]_D$ in 50% alcohol + 85·1° for $c = 2{\cdot}2315$.

When heated for 2 hours at 70° in methyl alcohol which was nearly saturated with hydrogen chloride, the dextrin was completely converted into methylglucoside. Initially excess of β-methylglucoside was formed, but, on continuing the reaction for 2½ hours, the equilibrium mixture was obtained, from which pure α-methylglucoside was isolated in the usual manner (m. p. 164°; OMe, 15·1%; $[\alpha]_D$ in water + 158·4°).

Examination of Dextrin II. Tetraglucosan.—This substance was produced in greatest yield when the polymerisation of β-glucosan was carried out in quantities of 20 g. at a time, a 600 c.c. flask being employed. The subsequent procedure was as described, and after removal of dextrin I, the more soluble products were fractionally precipitated with alcohol. Fractions showing similar rotatory power were mixed and again precipitated so that, by prolonged repetition of this process, the total product was ultimately separated into two portions which could not be further sub-divided. These showed, respectively, $[\alpha]_D$ + 60·7° and + 29·9° in aqueous solution and are indexed as *dextrin* II and *dextrin* III. Both substances were fine, white, hygroscopic powders and had the same composition as the parent glucosan. Dextrin II, when acetylated as already described, gave the same triacetate as dextrin I (Found : C, 50·2; H, 5·6; $CH_3 \cdot CO_2H$, 63·6%). The specific rotation and melting point also agreed within experimental error, and, on hydrolysing the acetate with sodium hydroxide, dextrin I was regenerated (Found : C, 44·5; H, 6·1; $[\alpha]_D$ + 81·5° for $c = 2{\cdot}14$ in water. Dextrin I requires C, 44·4; H, 6·2%; $[\alpha]_D$ + 83·9° for $c = 2{\cdot}08$).

Dextrin II was readily converted into methylglucoside. The solid was covered with methyl alcohol, and hydrogen chloride passed in from time to time until the dextrin dissolved, after which the solution was diluted with more alcohol and heated at 70°, polarimetric readings being taken every 15 minutes. In one hour the constant value $[\alpha]_D$ + 94·5° (calc. on the weight of glucoside formed) was reached and the product was then isolated as usual.

A crystalline mixture of α- and β-methylglucosides was thus obtained from which the pure α-form was separated by crystallisation from alcohol (Found: m. p. 165—166°; $[\alpha]_D$ + 157·2°; OMe, 15·6. α-Methylglucoside requires m. p. 165—166°; $[\alpha]_D$ + 157·5°; OMe, 15·9%).

When the above reaction was conducted at 50°, in place of 70°, and was arrested after 45 minutes, β-methylglucoside was the chief product and the α-form was present only to the extent of 20%.

Examination of Dextrin III. Triglucosan.—In all respects, save solubility and specific rotation, dextrin III resembled dextrin II. Like the latter, it yielded apparently the same triacetate as dextrin I (Found: C, 50·1; H, 5·6; $CH_3 \cdot CO_2H$, 62·3%). The specific rotation in aqueous alcohol was, however, + 74·2° in place of 78·9°, but this discrepancy appears to be due to a trace of impurity, as, on treatment with sodium hydroxide, dextrin I was regenerated. Dextrin III was also converted into methylglucoside in the usual way. The total crystalline product isolated showed $[\alpha]_D$ + 92·9° for $c = 1$ in methyl alcohol, and gave OMe, 15·3%. On crystallisation from absolute alcohol, pure α-methylglucoside displaying the standard constants was obtained. In this case also, when the reaction was restricted to heating at 50° for 1 hour, β-methylglucoside was the chief product.

Methylation of the Individual Dextrins.

As the methods adopted for the methylations have been described in previous papers from this laboratory, only significant results are now quoted.

Methylation of Dextrin I. Heptaglucosan.—The action of silver oxide and methyl iodide on a methyl-alcoholic solution was definitely arrested at the stage where two alkyl groups had been introduced per C_6 unit. Product: a colourless glass, easily powdered. $[\alpha]_D$ in chloroform + 76·0° for $c = 0·6035$ (Found: C, 50·65; H, 7·4; OMe, 32·4. $C_8H_{14}O_5$ requires C, 50·5; H, 7·4; OMe, 32·6%). The methyl sulphate reaction was more effective, repeated treatment with the reagents under conditions similar to those employed with inulin giving a product readily soluble in organic solvents and showing $[\alpha]_D$ in chloroform + 89·4° for $c = 2·745$. The methylation was, however, still incomplete, but approximated to the trimethyl stage [Found: C, 53·0; H, 7·5; OMe, 40·9. $(C_9H_{16}O_5)_n$ requires C, 52·9; H, 7·8; OMe, 45·5%]. No further purification was possible, as the compound, which was isolated as a glass readily convertible into a white powder, was exceedingly soluble in organic solvents with the exception of light petroleum. The molecular

weight, determined in benzene by the cryoscopic method, was 1446, whereas a hepta (trimethyl glucosan), $C_{63}H_{112}O_{35}$, requires 1428.

As, contrary to expectation, methyl alcohol containing 1% of hydrogen chloride proved to be without action on the compound, simultaneous hydrolysis and condensation was effected by heating for 15 hours at 70° with alcohol nearly saturated with the gas. No charring resulted from this drastic treatment and the specific rotation showed the usual characteristic rise and fall during the change. ($[\alpha]_D + 75{\cdot}0° \rightarrow 93{\cdot}7° \rightarrow 87{\cdot}5°$). The mixed glucosides were isolated by vacuum distillation as a colourless syrup (OMe, 50·4%) and were hydrolysed thereafter by means of 3% aqueous hydrochloric acid to give a solution of methylated glucoses showing $[\alpha]_D + 68{\cdot}4°$. A syrup was finally obtained on distillation showing OMe, 38·6% and yielding crystalline tetramethyl glucose on extraction with boiling light petroleum. The remaining sugars were di- and tri-methyl glucoses in unknown proportions.

Methylation of Dextrin II. Tetraglucosan.—As a result of three methylations by the methyl sulphate method, 18 g. of the dextrin were converted into 16·5 g. of a viscid syrup showing $[\alpha]_D + 66{\cdot}6°$ for $c = 3{\cdot}3335$ in chloroform, and having OMe, 39·5%. Two further methylations raised the methoxyl content to 41·6%, and four subsequent treatments gave the maximum value of 43·4%. The product was a glass possessing the customary solubilities [Found: C, 53·0; H, 7·8; OMe, 43·4. $(C_9H_{16}O_5)_n$ requires C, 52·9; H, 7·8; OMe, 45·5%].

Solvent.	c.	$[\alpha]_D$.
Methyl alcohol	1·3625	+68·7°
Acetone	1·958	70·5
Chloroform	2·900	61·2

Molecular weight, determined by the cryoscopic method in benzene solution, = 873. Tetra (trimethyl glucosan), $C_{36}H_{64}O_{20}$, requires 816.

When converted into the corresponding methylglucosides, as described in the case of the hepta-isomeride, the product on distillation showed in successive experiments OMe, 49·6, 49·7% and $[\alpha]_D + 100{\cdot}9°$ in water for $c = 1{\cdot}3016$. On hydrolysis with 4% aqueous hydrochloric acid the permanent value for the specific rotation was + 66·7°. The mixture of sugars thus obtained had OMe, 38·9% and was separated into (*a*) a fraction, soluble in ether, amounting to about two-thirds of the total, and (*b*) a fraction, consisting of the remainder, soluble in acetone but not in ether. From the soluble portion, tetramethyl glucose crystallised spontaneously and was identified by analysis and by determination of the physical constants. The uncrystallisable sugars were mixed,

converted into their methylglucosides, distilled in three fractions, and analysed. The methoxyl contents, in order of increasing volatility, were respectively 38·3, 44·8, and 53·4%, showing that the compounds were derived from a di- and a tri-methyl glucose. In no case did any of the sugars give a phenylosazone and the incompletely methylated forms were convertible into the stable variety of tetramethyl glucose in 80% yields.

It was necessary to ensure that the tetramethyl glucose isolated did not originate in degradation during the methylation of the original dextrin. The methylated dextrin was therefore extracted repeatedly with boiling light petroleum, but this did not cause any alteration in the methoxyl content. Further, when heated at 200°/0·2 mm., the methylated dextrin distilled very slowly, but analysis of the distillate showed that no tetramethyl methylglucoside was present.

Methylation of Dextrin III. Triglucosan.—Twenty grams, subjected to eleven successive treatments by the methyl sulphate reaction, gave 15·3 g. of a colourless glass convertible into a white solid [Found: C, 52·7; H, 7·8; OMe, 42·2. $(C_9H_{16}O_5)_n$ requires C, 52·9; H, 7·8; OMe, 45·5%].

Solvent.	*c.*	$[\alpha]_D$.
Chloroform	2·1035	+53·5°
Acetone	2·048	56·4
Methyl alcohol	1·753	52·8

The molecular weight, determined by the cryoscopic method in benzene, was 595. Tri(trimethyl glucosan), $C_{27}H_{48}O_{15}$, requires 612. When heated in a vacuum, approximately one-half of the material distilled at 180—200°/0·5 mm., but this result was evidently due to depolymerisation, as the distillate was a comparatively mobile syrup having $n_D = 1·4770$ and $[\alpha]_D$ in chloroform + 23·9°. The composition remained unaltered (OMe, 44·7%). The methylated dextrin, when subjected to the joint action of methyl alcohol and hydrogen chloride, was converted into the corresponding mixture of alkylated methylglucosides, the whole of the product being distillable, although over a wide temperature range. No fractionation was attempted, the total distillate being hydrolysed in one experiment by boiling with 4% aqueous hydrochloric acid. It is significant that when hydrolysis was complete the corrected specific rotation of the solution was + 65·3°, showing that the end products were the same as those obtained from the hepta- and tetra-isomerides. As before, the sugars thus obtained were divided into (*a*) a fraction soluble in ether which yielded crystalline tetramethyl glucose and a trimethyl glucose, and (*b*) a fraction soluble in acetone, but not in ether. The less soluble sugar, which was purified by dissolving

in chloroform and precipitating with ether, possessed the composition of a dimethyl glucose (OMe, 33·4%), but could not be obtained in a crystalline form and failed to give a phenylosazone. Both the di- and the tri-methyl glucose formed above belonged to the butylene-oxide series and polarimetric tests for the presence of γ-forms gave negative results.

Indirect Isolation of Polyglucosans in the Form of the Methylated Derivatives.

In place of separating the polyglucosans by precipitation and conducting the methylations in different experiments, an alternative is to alkylate the total polymerised material and thereafter to separate the methylated products. The latter method proved to be more effective, more economical, and more decisive.

Thirty grams of glucosan were polymerised, as described, in each experiment. By extraction of the product with boiling rectified spirit it was possible to remove unchanged glucosan together with the bulk of the dextrins of low molecular weight, leaving polymerides of high molecular weight undissolved, and, in this way, it was shown that both types of dextrin yielded normal triacetates. It was, however, preferable to methylate the total product directly, the methyl sulphate method being used throughout. A comparatively mobile syrup was thus obtained in good yield, 80 g. of glucosan giving 73 g. of methylated polymeride. On distillation at the Gaede pump, the product was separable as under :

Fraction I.	B. p. 135°/0·2 mm.	28 grams.	Trimethyl glucosan.
Fraction II.	B. p. 205—210°/0·2 mm.	17·1 grams.	Di(trimethyl glucosan).
Residue.		27·2 grams.	Poly(trimethyl glucosan).

In a second preparation, where more complete polymerisation was effected and where over-heating during distillation was avoided, 60 g. of glucosan yielded 55 g. of methylated product which in turn gave :

Trimethyl glucosan	9·41 grams	17%
Di(trimethyl glucosan)	12·98 ,,	23·6%
Poly(trimethyl glucosan)	31·77 ,,	57·8%

The monomeric trimethyl glucosan crystallised in the receiver; the dimeride was a pale yellow, clear, viscous syrup (n_D 1·4720), whilst the undistillable isomerides consisted of a glass.

Di(trimethyl glucosan).—The composition and physical constants of the distilled syrup showed very little variation in successive preparations [Found : C, 53·0, 52·9; H, 7·7, 7·9; OMe, 44·5; *M*, cryoscopic in benzene, 418. $(C_9H_{16}O_5)_2$ requires C, 52·9; H, 7·8; OMe, 45·6%; *M*, 408].

Solvent.	*c.*	$[\alpha]_D^{20°}$.
Chloroform	1·9515	+46·5°
Methyl alcohol	1·8790	48·3
Acetone	2·0040	51·8

Conversion into methylated methylglucosides. This reaction was accomplished by boiling with methyl alcohol nearly saturated with hydrogen chloride, the specific rotation, corrected for the change of concentration, becoming constant at + 110·0°. The mixed glucosides were isolated by distillation and although the liquid boiled over a wide range of temperature the product was collected as a single fraction (yield, 97%; n_D 1·4587). Under these conditions the distillate should have the same composition as trimethyl methylglucoside and this was the case (Found: C, 50·8; H, 8·5; OMe, 51·2. $C_{10}H_{20}O_6$ requires C, 50·8; H, 8·5; OMe, 52·5%). Separation of the constituents was effected by dissolving in water containing sodium bicarbonate and extracting repeatedly with chloroform. This treatment removed all glucosides containing four or more methoxyl groups per C_6 unit, lower methylated compounds remaining in the aqueous layer. The process can be applied quantitatively and, as in the present case yields are of special importance, the results of one exact experiment are quoted. 8·5483 Grams of di(trimethyl glucosan) gave 4·9161 g. of methylated glucosides extractable with chloroform, and 3·5824 g. were retained in the aqueous layer. The less soluble compound, when isolated, dissolved in ether, dried, and recovered, proved to be dimethyl methylglucoside showing $[\alpha]_D$ + 108·4° in methyl alcohol, and n_D 1·4743 (Found: C, 48·7; H, 8·2; OMe, 41·2. Calc. for $C_9H_{18}O_6$, C, 48·8; H, 8·1; OMe, 41·8%).

Analysis of the syrup extracted with chloroform having shown that it consisted essentially of tetramethyl methylglucoside together with a little trimethyl methylglucoside, the mixture was hydrolysed to give the corresponding sugars. On repeating the extraction with chloroform, only tetramethyl glucose passed into the lower layer, whilst trimethyl glucose was retained in the aqueous layer. The tetramethyl glucose, when recovered, purified by distillation and recrystallised as usual, displayed the correct melting point and rotation (Found: C, 50·8; H, 8·4; OMe, 52·0. Calc. for $C_{10}H_{20}O_6$, C, 50·8; H, 8·5; OMe, 52·5%). In this way, 3·2457 g. of pure sugar were obtained from 4·4717 g. of the mixed glucosides. The small amount of trimethyl glucose isolated shows that this sugar cannot be regarded as a definite molecular product but originates in unpolymerised trimethyl glucosan. Neglecting this by-product and small undistilled residues, the relative yields of the hydrolysis sugars, calculated as the corresponding glucosides, become:

	Found.	Calc. for equal molecules.
Dimethyl methylglucoside	46·6	47·1%
Tetramethyl methylglucoside	53·4	52·9%

Examination of Methylated Polyglucosans.—The non-volatile residue left when di(trimethyl glucosan) was separated by distillation constituted the main product of the methylation of polymerised glucosan. After solution in ether, filtration and removal of the solvent, the mixture of higher polymerides was obtained as a clear glass. The carbon content was low, although the composition was uniform in different preparations [Found : C, 52·4, 52·4; H, 7·6, 7·8; OMe, 44·4, 45·2. $(C_9H_{16}O_5)_n$ requires C, 52·9; H, 7·8; OMe, 45·5%]. As, from its method of preparation, the material consisted of all polymerides higher than the dimeride, no molecular weights were determined.

Solvent.	*c.*	$[\alpha]_D$.
Chloroform	1·850	+63·3°
Acetone	2·266	66·6
Methyl alcohol	1·755	64·4

Conversion by the action of acid methyl alcohol into the mixture of methylated glucosides gave a 95% yield of a colourless syrup, which was distilled under 0·4 mm. and collected in one portion without fractionation. The average composition of the total distillate should be the same as that of trimethyl methylglucoside, but although this held approximately, all the values were low (Found : C, 50·4; H, 8·3; OMe, 50·6. Calc. for $C_{10}H_{20}O_6$, C, 50·9; H, 8·5; OMe, 52·5%). On separating the constituent glucosides by extraction of an aqueous solution containing sodium bicarbonate with chloroform, the syrup recovered from the extract weighed 69% of the original total, and the remaining 31% was recovered from the water. The former was hydrolysed with 8% hydrochloric acid to give the corresponding methylated glucoses, which were isolated in 94% yield. Analysis of the distilled sugars showed that tri- and tetramethyl glucose were present in equimolecular proportions (Found : C, 49·9; H, 8·2; OMe, 46·8. Calc., C, 49·8; H, 8·3; OMe, 47·3%). Separation of the sugars was effected by the method of chloroform extraction, 11·176 g. of the mixture giving 5·300 g. of crystalline tetramethyl glucose displaying the correct analytical figures and constants. The less soluble sugar was recovered from the water, distilled as a viscid syrup and identified as a trimethyl glucose (Found : C, 48·6; H, 7·95; OMe, 41·4. Calc. for $C_9H_{18}O_6$, C, 48·6; H, 8·1; OMe, 41·8%). The specific rotation in chloroform solution was + 72·5° but, in order to identify it completely, the sugar was converted successively into the diacetate, the monoacetobromo-derivative, and finally into the corresponding trimethyl β-methylglucoside. These steps were controlled by blank experiments in which authentic 2 : 3 : 5-trimethyl glucose was used, and the optical changes were parallel throughout. On nucleation with

2 : 3 : 5-trimethyl β-methylglucoside, the product crystallised and was purified as usual from light petroleum. The m. p., refractive index and specific rotation in methyl alcohol were correct (Found: C, 50·7; H, 8·5; OMe, 51·9. Calc. for $C_{10}H_{20}O_6$, C, 50·8; H, 8·5; OMe, 52·5%). The combined results show that the sugars extractable by chloroform from aqueous solution are 2 : 3 : 5 : 6-tetramethyl glucose and 2 : 3 : 5-trimethyl glucose in equimolecular proportion.

The lower methylated glucoside retained in aqueous solution after extraction of the tetra- and tri-methyl methylglucosides with chloroform consisted of a viscid syrup (n_D 1·4779, $[\alpha]_D$ in methyl alcohol + 106·2°). Although with material of this nature vacuum distillation is difficult, this purification was undertaken to obtain more accurate analytical figures. Pure dimethyl methylglucoside was thus obtained as the main fraction (b. p. over 190°/0·4 mm.; n_D 1·4743) (Found: C, 48·55; H, 8·2; OMe, 40·8. Dimethyl methylglucoside, $C_9H_{18}O_6$, requires C, 48·6; H, 8·1; OMe, 41·8%). The undistillable residue was a glass and consisted essentially of monomethyl methylglucoside (Found: C, 45·7; H, 7·2; OMe, 28·9. Calc. for $C_8H_{16}O_6$, C, 46·15; H, 7·7; OMe, 29·8%). About 5% of the total sugars formed from the dextrin consisted of this material, which almost certainly originates in incomplete methylation.

Attempts to establish the constitution of the dimethyl glucose isolated in the present section of the research led to no final conclusions. The sugar failed to crystallise and formed no phenylosazone; it also failed to enter into condensation with acetone when dissolved in this reagent containing 0·2% of hydrogen chloride, but reacted when the concentration of acid was raised to 1·3%. No definite benzylidene derivative could be prepared, either from the sugar or from its methylglucoside, but the combined results, although not conclusive, favour the view that of the two alternatives, 2 : 3- or 2 : 5-dimethyl glucose, the latter is more probable.

We desire to express our indebtedness to the Department of Scientific and Industrial Research for a Research Assistantship granted to one of us.

UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS. [*Received, October 16th,* 1925.]

CCCCV.—*The Electrical Conductivities of Hydrogen Chloride and Potassium Chloride in Water and Acetone–Water Mixtures.*

By Thomas Kerfoot Brownson and Frank Maurice Cray.

The electrical conductivities of a large number of salts in acetone-water mixtures have been measured, especially by Jones and his co-workers (Jones, Bingham, and McMaster, *Z. physikal. Chem.*, 1906, **57**, 193, 257; Jones and Mahin, *Carnegie Institute of Washington Publication*, 1913, **180**, 193).

The present investigation of the electrical conductivities of hydrogen chloride and potassium chloride in water and acetone–water mixtures was carried out to obtain information in connexion with a research upon the preparation of solutions of standard hydrogen-ion concentration and the measurement of indicator ranges in an acetone–water mixture containing 10% by volume of water (Cray and Westrip, *Trans. Faraday Soc.*, 1925, **21**). Owing to the nature of the investigation, it was necessary to obtain a high order of accuracy.

A detailed survey has been made of the alteration in the electrical conductivities and the degree of dissociation of these electrolytes over a wide range of dilutions in solvents ranging from pure water to the acetone–water mixture containing only 5 volumes of water in 100 volumes of the mixed solvent. Conductivity measurements have been made for hydrogen chloride in water and eight mixtures of acetone–water and for potassium chloride in water and six acetone–water mixtures at 20° and 25° and at dilutions ranging from 10 to 10,000 litres per gram-molecule.

Experimental.

Materials.—Acetone was dehydrated over fused calcium chloride and distilled fractionally at least twice immediately before use, care being taken to avoid contamination from the air. The acetone distilled between 56·2° and 56·3° at 760 mm., and none with a specific conductivity greater than $0{\cdot}5 \times 10^{-7}$ mho. at 20° was used. This acetone compares favourably with that obtained by other investigators (*e.g.*, Dutoit and Levier, *J. Chim. Phys.*, 1905, **3**, 435; κ $0{\cdot}5$—$2{\cdot}0 \times 10^{-7}$ mho. at 20°. Benz, Dissertation, Lausanne, 1905; κ $0{\cdot}22 \times 10^{-7}$ mho. at 18°).

The water was prepared from high grade distilled water by a double distillation and had a specific conductivity less than $1{\cdot}2 \times 10^{-6}$ mho at 20°.

The hydrochloric acid was prepared in normal solution and its strength determined gravimetrically from time to time.

The potassium chloride (A.R. quality) was recrystallised three times from conductivity water, heated for some hours at 120°, and kept in a vacuum desiccator. Standard solutions were made up as required by direct weighing and standardised against silver nitrate.

Preparation of Solutions.—All mixtures of acetone and water were made up to contain the specified volume of water in 100 volumes of the mixed solvent, the final volume adjustment being carried out at 15°. Great care was paid to this dilution on account of the considerable contraction in volume (Reilly, *Proc. Roy. Dublin Soc.*, 1919, **15**, 43) and change in temperature which take place upon mixing acetone and water.

In each series of conductivity measurements, the most concentrated solution and occasionally the more dilute solutions of hydrogen chloride and potassium chloride were prepared in a manner similar to the above, the requisite volume of acid or salt solution replacing an equivalent volume of water. Subsequent dilution was carried out using specially standardised flasks and pipettes. This method was considered preferable to direct weighing on account of the volatility of the acetone.

All measurements were carried out on the same day as the solutions were made up and these were kept in the dark until actually required.

The range of dilutions covered in the case of potassium chloride was limited by its sparing solubility, especially in solvents rich in acetone. The electrical conductivities were measured at dilutions up to 10,000 litres except in solvents with a high water content; the highest dilution was then 2,500.

Apparatus.—The usual type of Kohlrausch apparatus modified as described below was used with a thermionic valve oscillator as the source of alternating current and with the telephones across the ends of the bridge wire (Schlesinger and Reed, *J. Amer. Chem. Soc.*, 1919, **41**, 1727). The bridge wire, calibrated by the method of Strouhal and Barus and of accurately measured resistance, could be extended at either end by means of non-inductive standard resistance coils. The other arms of the bridge contained a standard resistance box and the electrolytic cell respectively, whilst two variable air-condensers were arranged in parallel, so that they could be connected in parallel across either arm of the bridge as required, in order to balance the capacities in the system.

All connecting wires were of stout copper and of known resistance, which was corrected for when necessary.

The thermostats were regulated to $\pm 0{\cdot}05°$ by means of Lowry regulators with electrical control and all metal parts were earthed.

Source of Current.—Taylor and Acree (*J. Amer. Chem. Soc.*, 1916, **38**, 2415) have shown that the resistance of an electrolyte in aqueous solution measured between platinised electrodes of half-inch diameter alters with frequency up to 600 cycles, but that there is no change of resistance at high frequencies, which were investigated up to 2,000 cycles.

Preliminary work on these acetone–water mixtures with an induction coil as the source of alternating current showed that accurate reproducible results were unobtainable on account of the lowness and inconstancy of the frequency together with the unsymmetrical and irregular nature of the current. This source of current was therefore discarded in favour of a Sullivan thermionic valve oscillator, the frequency of the alternating current being readily adjustable by means of the anode condenser. The frequency used in this investigation was 1060 cycles, which was sufficiently high to reduce the possibility of polarisation in the cell and also gave a note readily detected in the telephones.

A cathode ray oscillograph was used to ascertain whether the current had a pure sinusoidal form.

No difficulty was experienced even at the highest dilutions in obtaining an excellent minimum in the telephones, when the resistances and capacities were accurately balanced.

Conductivity Cells.—Taylor and Acree (*loc. cit.*) have shown that in aqueous solution, whilst there is no change of resistance with change in frequency when platinised electrodes are used at frequencies above 600 cycles, there is a fall in resistance with increasing frequency when plain platinum electrodes are used. When these results are extrapolated to infinite frequency, the resistance measured with plain electrodes is identical with that found at the lower frequencies with platinised electrodes.

A preliminary survey of the behaviour of electrodes in acetone–water mixtures showed that the resistances of solutions measured with plain electrodes were higher than the resistances of the same solutions measured with platinised electrodes, but that the discrepancy between them decreased as the resistance of the solution being measured increased. Thus, in the acetone–water mixture containing 10% by volume of water, the results obtained at the higher dilutions with either electrode surface were substantially identical.

The possibility of error due to the catalytic action of the platinum black on the acetone was investigated in a series of experiments in which the specific conductivities of hydrogen chloride solutions

containing one gram-molecule in 20, 500 and 5,000 litres of 95 : 5 acetone–water were measured at 20° for periods up to 50 minutes, during which time the current was passing through the cell.

The maximum alteration in specific conductivity of these solutions over this period was $\pm$ 0·15% at the highest dilution, but as the changes were in the direction of both increased and decreased specific conductivity, any alteration was ascribed to temperature fluctuations and experimental error in determining the bridge setting.

The conclusion is drawn that the use of platinised platinum electrodes is not attended by objection in acetone–water mixtures on account of catalytic action of platinum black on the solvent.

Three cells having cell constants 0·5703, 0·4686, and 0·1686 were used for the measurement of the specific conductivities of the electrolyte solutions. The standard solution for determining these constants was 0·02*N*-aqueous potassium chloride; its specific conductivity at 25° being taken from the results of A. C. Melcher (Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 454). The cell constants were checked at frequent intervals during the course of the research and wherever possible the conductivity of a solution was measured in two cells having respectively low and high cell constants.

The cells were all of the same type, consisting of a tubular borosilicate glass vessel, closed by means of a stopper and fitted in each case with lightly platinised platinum disk electrodes, 1 cm. in diameter, mounted vertically on stout platinum leads, which were carried through the walls of the vessel into side tubes containing mercury.

Solvent Correction and Calculation of the Equivalent Conductivity at Infinite Dilution.—The corrections which should be applied to values of the specific conductivities of electrolytes on account of the conductivity of the solvent itself have been discussed by several investigators. Kendall (*J. Amer. Chem. Soc.*, 1917, **39**, 7) has summarised the position and concludes that, if the solvent is of sufficiently high degree of purity, no correction need be applied in the case of acids stronger than acetic acid throughout the ordinary range of dilution, but that where the electrolyte is the salt of a strong acid and strong base, substantially accurate values are obtained by the procedure of Kohlrausch, namely, direct subtraction of the whole of the solvent conductivity.

The dissociation constant calculated for hydrogen chloride from conductivity measurements falls as the percentage of acetone in the mixed solvent increases, but even in the solvent containing 5 volumes of water in 100 volumes of acetone–water it is approximately 6×10^{-4} at 25° compared with $1{\cdot}8 \times 10^{-5}$ at 25° for acetic

acid in water. Consequently, no correction has been applied on account of the conductivity of the solvent itself to the values obtained for hydrogen chloride in these acetone–water mixtures, but in the case of potassium chloride the whole of the solvent conductivity has been subtracted.

In all cases the specific conductivity of the solvent was small in comparison with that of the electrolytes, even at the highest dilutions.

The values for the equivalent conductivity at infinite dilution have been calculated by the method suggested by Washburn (*J. Amer. Chem. Soc.*, 1918, **40**, 122) from the equivalent conductivities at the highest dilutions measured, the value of the mass-action expression $\lambda_v^2/\lambda_\infty(\lambda_\infty - \lambda_v)v$ being plotted against the concentration for various assumed values of λ_∞ and that figure for λ_∞ being taken as the most probable which led to no abrupt rise or fall in the curve at the highest dilution.

The degree of dissociation of the electrolytes has been obtained from the expression $\alpha = \lambda_v/\lambda_\infty$, no account being taken of the change of viscosity with dilution.

Results.

The influence of variation in the composition of the solvent will be shown to be extremely marked in acetone–water mixtures of high acetone content, especially in the case of the more concentrated electrolyte solutions. Thus, alteration in the water content from 5 to 10% by volume is accompanied by a 100% change in the equivalent conductivity at dilution $v = 50$ and by a 2·5% change at $v = 10{,}000$. The measurements in all acetone–water mixtures were repeated several times with different samples of acetone. Thus, in the case of hydrogen chloride in the solvent containing 10% by volume of water, nine separate series of measurements at all dilutions were made with different samples of acetone. The results given in all cases are the mean values. In the solvent mentioned, the variation from the mean of these nine series of results over all dilutions was $\pm$ 0·5% and the reproducibility in solvents richer in water was of considerably higher degree of accuracy. In the solvent containing 50% by volume of water, the variations were only $\pm$ 0·2%, the results in the different series being in the same relative order at all dilutions.

A series of at least ten measurements with different bridge settings was made for every solution, the maximum divergence from the mean being generally less than $\pm$ 0·05%.

Owing to the considerable difficulties in obtaining really accurate values in pure acetone, due particularly to the marked effect of

Table I.

Equivalent conductivities of hydrogen chloride in acetone–water mixtures at 25°.

	Volume % of water								
v	5	10	20	35	50	65	80	90	100
10	—	20·89	51·49	99·44	149·7	202·1	270·1	321·3	389·9
20	13·76	—	—	—	—	—	—	—	—
25	—	30·81	63·93	110·1	158·0	211·0	281·6	332·0	401·0
50	19·70	38·93	72·88	116·9	162·7	215·9	286·8	336·0	406·4
100	26·15	48·42	80·55	122·6	167·3	219·7	290·3	341·0	411·0
250	37·50	63·40	91·40	129·0	172·5	224·3	293·3	344·2	415·3
500	48·08	73·96	96·55	132·2	174·2	225·8	295·0	346·6	418·0
1,000	60·39	83·13	100·8	133·8	175·4	226·6	296·4	348·0	419·5
2,500	77·47	93·16	104·9	135·8	175·9	227·3	297·3	348·9	420·7
5,000	88·41	98·22	106·4	137·0	176·3	227·5	—	—	—
10,000	97·61	101·5	107·7	137·7	176·5	—	—	—	—
∞	(112·2)	(105·5)	(109·1)	(138·5)	(176·8)	(227·8)	(297·9)	(349·6)	(422·0)
κ of solvent in mho × 10^{-6}	0·054	0·11	0·20	0·30	0·44	0·55	0·75	0·85	1·0

Table II.

The equivalent conductivities of hydrogen chloride in acetone–water mixtures at 20°.

	Volume % of water.						
v.	5.	10.	20.	35.	50.	80.	100.
10	—	19·70	47·86	90·77	135·7	247·0	362·5
20	13·21	—	—	—	—	—	—
25	—	28·77	59·02	100·4	143·1	257·6	372·5
50	18·97	36·55	67·20	106·4	147·1	262·4	376·9
100	25·05	45·37	74·24	111·7	151·1	265·1	380·6
250	35·90	59·29	84·10	117·3	155·6	267·8	384·5
500	45·88	69·00	88·60	119·9	157·1	269·4	387·2
1,000	57·54	77·28	92·35	121·3	158·1	270·4	388·1
2,500	73·55	86·50	96·10	123·0	158·6	271·3	389·5
5,000	83·80	91·25	97·25	123·7	158·9	—	—
10,000	92·56	94·40	98·40	124·5	159·1	—	—
∞	(106·4)	(98·0)	(99·7)	(125·2)	(159·3)	(272·0)	(390·6)
κ of solvent in mho × 10^{-6}	0·049	0·09	0·18	0·26	0·40	0·68	0·90

Table III.

The equivalent conductivities of potassium chloride in acetone–water mixtures at 25°

	Volume % of water.						
v.	5.	10.	20.	35.	50.	65.	100.
50	—	—	53·20	59·75	67·45	80·40	138·6
100	—	58·90	60·32	64·47	70·80	82·09	141·6
250	—	72·95	68·50	68·49	74·02	85·20	145·2
500	—	82·50	73·20	70·95	75·70	86·00	146·7
1,000	98·39	89·00	76·54	73·00	76·61	86·70	147·7
2,000	108·1	—	—	—	—	—	—
2,500	—	98·80	79·80	74·65	78·00	87·75	149·1
5,000	117·9	99·15	81·30	75·90	78·64	88·40	—
10,000	122·4	101·3	82·80	—	—	—	—
∞	(127·7)	(103·7)	(84·50)	(77·30)	(79·40)	(89·10)	(150·1)
κ of solvent in mho × 10^{-6}	0·054	0·11	0·20	0·30	0·44	0·55	1·0

TABLE IV.

The equivalent conductivities of potassium chloride in acetone–water mixtures at 20°.

	Volume % of water.						
v.	5.	10.	20.	35.	50.	65.	100.
50	—	—	48·81	53·81	60·00	71·27	125·5
100	—	55·05	55·20	57·81	63·02	72·78	128·2
250	—	68·13	62·60	61·39	65·80	75·28	131·0
500	—	76·40	66·85	63·60	67·10	76·05	132·1
1,000	92·31	82·28	69·91	65·42	68·01	76·70	132·9
2,000	101·5	—	—	—	—	—	—
2,500	—	88·40	72·75	66·60	69·03	77·50	134·3
5,000	110·2	91·70	74·00	67·70	69·65	78·00	—
10,000	114·3	93·60	75·30	—	—	—	—
∞	(119·1)	(95·7)	(76·90)	(68·90)	(70·3)	(78·60)	(135·2)
κ of solvent in mho $\times 10^{-6}$	0·049	0·09	0·18	0·26	0·40	0·50	0·90

TABLE V.

The equivalent conductivities of hydrogen chloride in water at 18° *and* 25° *and of potassium chloride at* 25°.

	Hydrogen chloride.				Potassium chloride. 25°.		
	18°.		25°.				
v.	This research.	Goodwin and Haskell (interpolated).	This research.	Bray and Hunt (interpolated).	This research.	Melcher.	Lorenz (interpolated).
10	351·7	351·4	389·9	390·4	—	129·0	—
25	362·0	—	401·0	400·7	135·4	—	135·1
50	364·9	365·5	406·4	406·7	138·6	138·65	138·6
100	368·5	369·2	411·0	411·6	141·6	141·4	141·6
250	372·3	373·6	415·3	416·4	145·2	—	144·75
500	374·9	375·0	418·0	418·6	146·7	146·5	146·55
1000	375·8	375·9	419·5	419·0	147·7	—	147·75
2500	377·2	—	420·7	—	149·1	—	149·22
∞	(378·2)	—	(422·0)	—	(150·1)	(150·6)	—

even the slightest trace of water, this solvent has not been studied in this investigation. Results can be extrapolated for pure acetone from the values given, but it is hoped in the future to investigate the problem experimentally, as the only data available are very incomplete (Carrara, *Gazzetta*, 1897, **27**, i, 207; Sackur, *Ber.*, 1902, **35**, 1248).

The values for hydrogen chloride are all observed values, being uncorrected, and those for potassium chloride corrected by subtraction of the solvent conductivity. Kendall (*J. Amer. Chem. Soc.*, 1917, **39**, 7) gives 379·1 as the most probable value of λ_∞ for hydrogen chloride in water at 18°, and 422·7 at 25°.

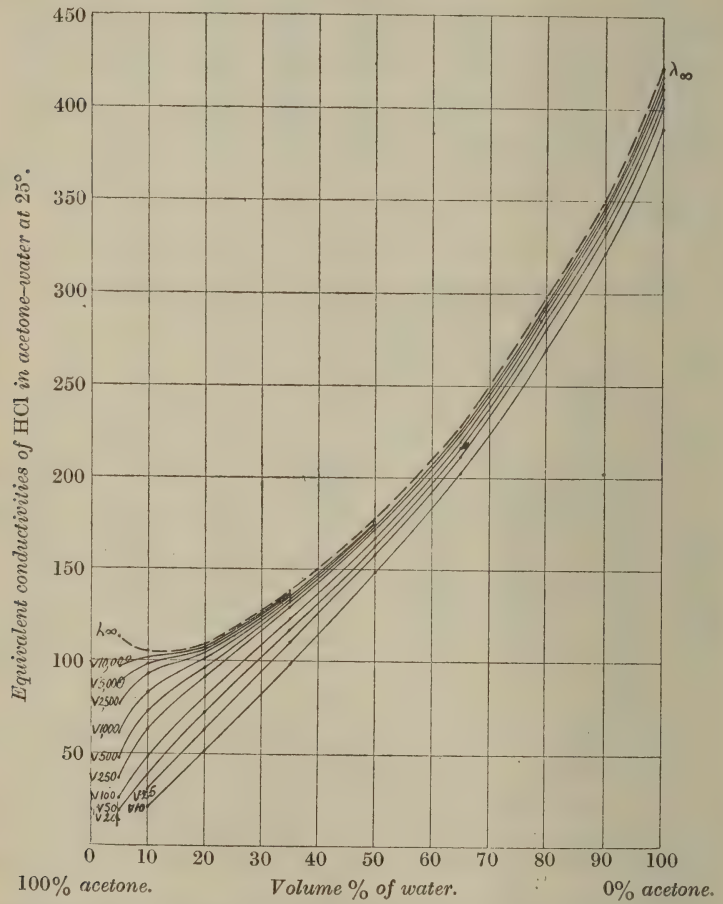
References.—Goodwin and Haskell, *Physical Rev.*, 1904, **19**, 380. Bray and Hunt, *J. Amer. Chem. Soc.*, 1911, **33**, 781. Melcher,

see Noyes and Falk, *ibid.*, 1912, **34**, 154. Lorenz, *Z. angew. Chem.*, 1921, **116**, 161.

Discussion.

The Influence of the Solvent on the Equivalent Conductivity of Potassium Chloride and Hydrogen Chloride.—The influence of the

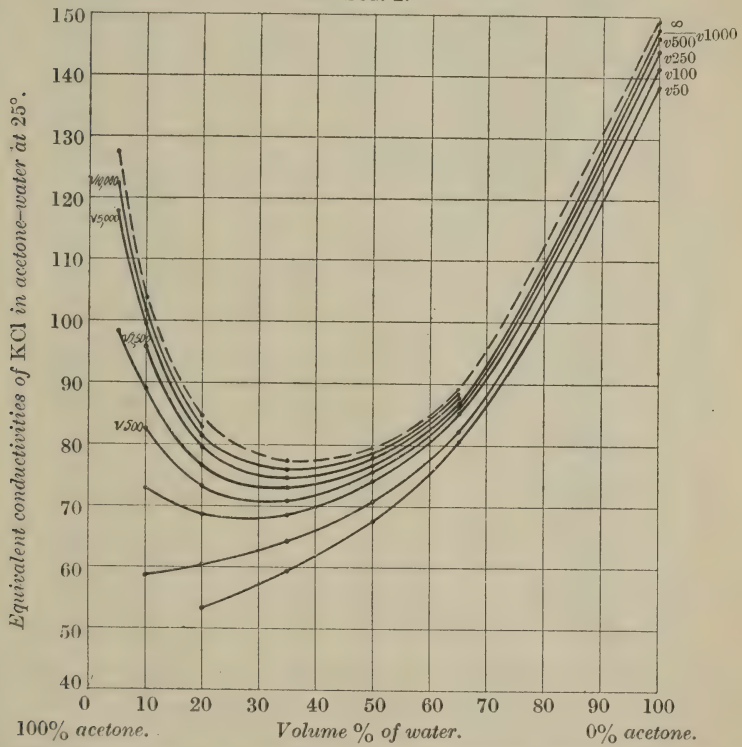
FIG. 1.



solvent upon the equivalent conductivity of hydrogen chloride in these acetone–water mixtures is extremely marked (Fig. 1). According to the classical theory of electrolytic dissociation, this arises from two causes; first, the effect of the solvent upon the migration velocities of the individual ions and secondly, upon the degree of dissociation of the electrolyte. The equivalent conductivity at infinite dilution falls rapidly as water is replaced by acetone up to

about 85% of acetone by volume, followed by an increase of conductivity in acetone–water mixtures richer in acetone. The effect of alteration in the degree of dissociation of the electrolyte is shown by the equivalent conductivities at finite dilutions and accounts for the points of inflexion in the equivalent conductivity–composition of the solvent curves (Fig. 1) at the acetone–water mixture containing 10% by volume of water, where the solvent has a marked effect upon the degree of dissociation of the electrolyte (Fig. 3).

FIG. 2.

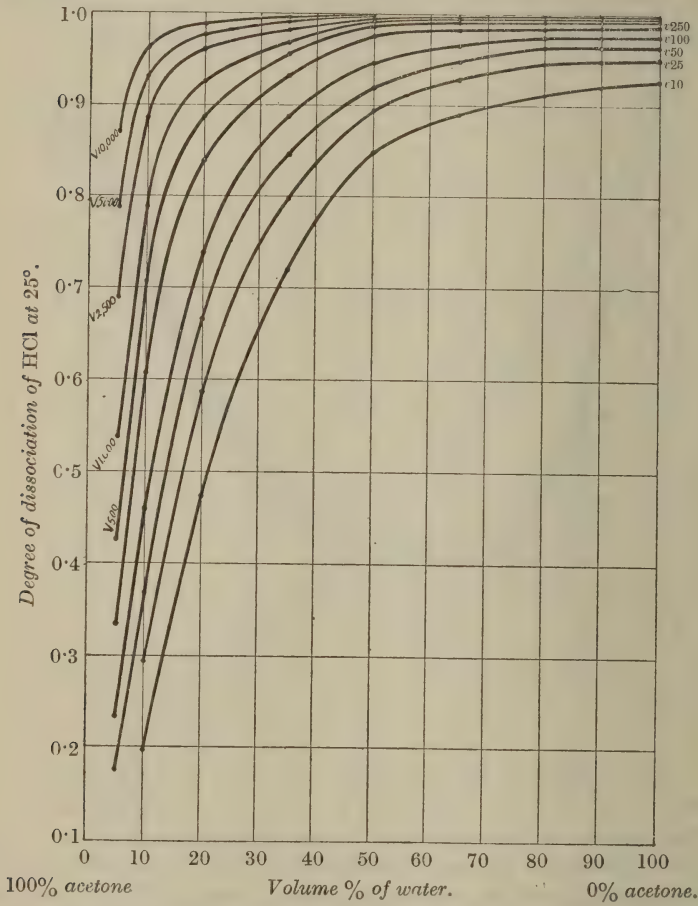


The nature of the equivalent conductivity–composition of the solvent curves for potassium chloride in acetone–water mixtures differs greatly from the case of hydrogen chloride. The equivalent conductivity at infinite dilution falls to a minimum in the solvent containing 40% by volume of water (Fig. 2), but owing to the effect of the fall in degree of the dissociation of this electrolyte with increase in acetone content of the solvent (Fig. 4), this minimum changes with dilution and indeed in the case of dilutions $v = 50$; $v = 100$, no minimum is observable within the limited range of acetone–water mixtures which can be studied at those concen-

trations on account of the low solubility of potassium chloride in mixtures rich in acetone.

Numerous investigators have attempted to show the dependence of the equivalent conductivity at infinite dilution on the physical properties of the solvent. Hartley, Thomas, and Applebey (J.,

FIG. 3.



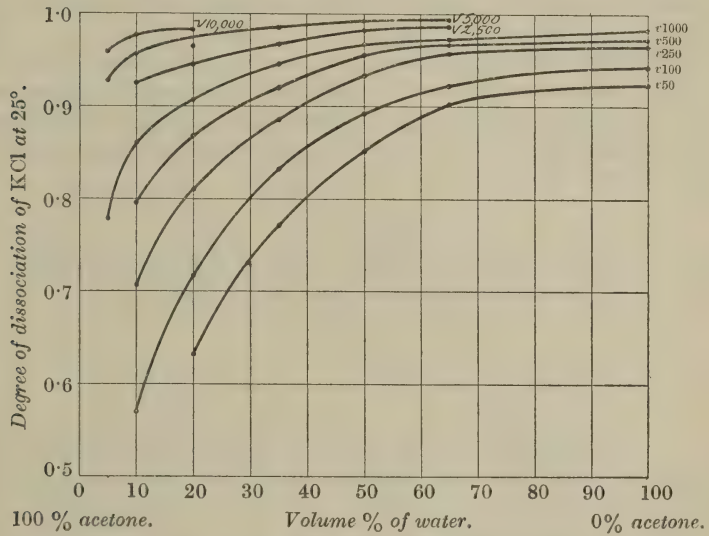
1908, **93**, 538), on the assumption of the applicability of Stokes' law to an ion moving with a spherical solvent atmosphere surrounding it, have shown that if the ionic radii of the anion and kation respectively do not vary with the composition of the solvent, then $\lambda_\infty \eta$ = constant, where η is the viscosity of the solvent.

Walden (*Z. physikal. Chem.*, 1906, **52**, 242; 1911, **78**, 273, 278, etc.) has shown that the product $\lambda_\infty \eta$ is constant and independent

of the temperature for tetramethylammonium iodide, tetrapropylammonium iodide, potassium iodide and other organic salts in a large number of organic solvents, but he has also shown that solvents with large association factors and high dielectric constants give variations from this rule. Creighton (*J. Franklin Inst.*, 1919, **187**, 33) found that deviations were shown by trimethyl-*p*-tolylammonium iodide in several organic solvents.

The viscosities of acetone–water mixtures rise to a maximum in the solvent containing approximately 60% by volume of water (Davis, Hughes, and Jones, *Z. physikal. Chem.*, 1913, **85**, 535), whereas the equivalent conductivity at infinite dilution of potassium

FIG. 4.



chloride in acetone–water mixtures has been shown in the present research to be a minimum in the solvent containing 40% of water by volume. No constancy of the expression $\lambda_\infty \eta$ can be expected. The equivalent conductivity of the electrolyte at infinite dilution is therefore dependent not only on the viscosity of the solvent but also on its other physical properties, for example, its state of association and dielectric constant.

In aqueous solutions the conductivity of hydrogen chloride is exceptional owing to the high value of the mobility of the hydrogen ion. In acetone–water mixtures of high acetone content, however, the mobility of the hydrogen ion does not differ greatly from that of the potassium ion, as the equivalent conductivity of hydrogen chloride at infinite dilution is only slightly higher than that of

potassium chloride in the acetone–water mixture containing 10% by volume of water. In the solvent containing 5% by volume of water, it is actually smaller.

The Influence of the Solvent on the Degree of Dissociation.—The influence of the solvent upon the degree of dissociation of electrolytes has been formulated in the well-known Nernst–Thomson rule.

Bruhl (*Z. physikal. Chem.*, 1899, **30**, 1) has pointed out that no absolute proportionality can exist between the dissociating power and the dielectric constant of the solvent, as the latter varies greatly with temperature and also with frequency.

The values of the degree of dissociation of hydrogen chloride and potassium chloride calculated from the expression $\alpha = \lambda_v/\lambda_\infty$ are in Table VI, and the influence of the solvent is shown in Figs. 3 and 4.

The influence of temperature upon the degree of dissociation of the electrolytes in acetone–water mixtures is, as would be expected, more marked the greater the concentration and the smaller the degree of dissociation of the electrolyte and the dielectric constant of the solvent.

TABLE VI.

The degree of dissociation of hydrogen chloride and potassium chloride in acetone–water mixtures at 20° and 25°.

Hydrogen Chloride.

	Volume % of water													
	5		10		20		35		50		80		100	
v	20°	25°	20°	25°	20°	25°	20°	25°	20°	25°	20°	25°.	20°.	25°
10	—	—	0·201	0·198	0·480	0·472	0·725	0·718	0·852	0·847	0·908	0·906	0·928	0·925
25	—	—	0·295	0·292	0·592	0·586	0·802	0·795	0·899	0·894	0·947	0·945	0·953	0·950
50	0·178	0·176	0·373	0·369	0·674	0·668	0·850	0·844	0·923	0·920	0·965	0·963	0·965	0·963
100	0·236	0·233	0·463	0·459	0·744	0·738	0·892	0·885	0·949	0·946	0·975	0·974	0·974	0·974
250	0·337	0·334	0·605	0·601	0·843	0·838	0·937	0·931	0·977	0·975	0·984	0·984	0·984	0·984
500	0·431	0·428	0·704	0·701	0·889	0·885	0·958	0·954	0·986	0·985	0·991	0·990	0·991	0·991
1,000	0·541	0·538	0·789	0·788	0·926	0·924	0·969	0·966	0·993	0·992	0·994	0·995	0·994	0·994
2,500	0·691	0·690	0·883	0·883	0·964	0·962	0·982	0·980	0·996	0·995	0·997	0·998	0·997	0·997
5,000	0·787	0·788	0·931	0·931	0·975	0·975	0·989	0·989	0·998	0·997	—	—	—	—
10,000	0·870	0·870	0·963	0·962	0·987	0·987	0·994	0·994	0·999	0·998	—	—	—	—

Potassium Chloride.

	Volume % of water.													
	5		10		20		35		50		65		100	
v	20°	25°	20°	25°	20°	25°	20°	25°	20°	25°	20°	25°	20°	25°
50	—	—	—	—	0·635	0·630	0·781	0·773	0·853	0·850	0·907	0·902	0·928	0·923
100	—	—	0·575	0·568	0·718	0·714	0·839	0·834	0·896	0·892	0·926	0·921	0·948	0·943
250	—	—	0·712	0·704	0·814	0·811	0·891	0·886	0·936	0·932	0·958	0·956	0·969	0·967
500	—	—	0·798	0·796	0·869	0·866	0·923	0·918	0·954	0·954	0·968	0·965	0·977	0·977
1,000	0·775	0·770	0·860	0·858	0·909	0·906	0·949	0·944	0·967	0·965	0·976	0·973	0·983	0·983
2,500	—	—	0·924	0·924	0·946	0·944	0·967	0·966	0·982	0·982	0·986	0·985	0·994	0·993
5,000	0·925	0·923	0·958	0·956	0·962	0·962	0·983	0·982	0·991	0·990	0·992	0·992	—	—
10,000	0·960	0·958	0·978	0·977	0·979	0·980	—	—	—	—	—	—	—	—

The values of the Ostwald expression, $\alpha^2/(1 - \alpha)v$, show considerable alteration with dilution in water or acetone–water solvents and

in no case is a true constant obtained, but in mixtures rich in acetone the change with dilution is much less marked.

Summary.

(1) The electrical conductivities of hydrogen chloride and potassium chloride have been measured over a wide range of dilution at 20° and 25° in acetone–water mixtures containing from 5 to 100% of water by volume.

The equivalent conductivity of hydrogen chloride at infinite dilution falls sharply to a minimum in the solvent containing about 85% of acetone, after which the change is small, an increase being noticed in solvents very rich in acetone. In other solutions, the equivalent conductivity falls as the acetone content increases, as the result of the influence of the solvent upon the degree of dissociation of the electrolyte as well as upon the migration velocities of the individual ions.

The equivalent conductivity of potassium chloride at infinite dilution falls to a well-defined minimum in the solvent containing approximately 40% by volume of water, but at other dilutions, owing to the change in degree of dissociation of the electrolyte, this minimum shifts and in more concentrated solutions, $v = 100$ and $v = 50$, no minimum is observable in any acetone–water mixture in which the solubility of this electrolyte allows the measurement to be made.

(2) It is shown that the use of platinised platinum electrodes is not attended by error due to catalytic influence upon the acetone in the mixed solvents studied.

(3) The influence of temperature upon the degree of dissociation of these electrolytes is more marked the higher the acetone content of the solvent and the higher the concentration of the solution.

(4) The Ostwald dilution law does not hold fully in any acetone–water mixture investigated, but, as the acetone content increases, gives values more nearly approaching a constant at all dilutions.

We wish to express our indebtedness to Dr. G. Rotter, C.B.E., and Dr. J. N. Pring for their interest in this work, which is published by permission of the Director of Artillery, War Office.

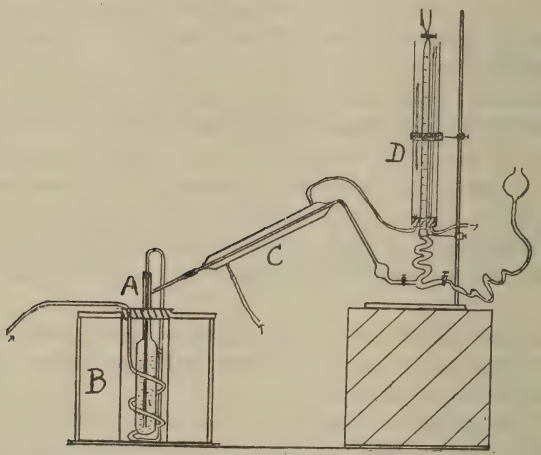
Research Department,
Royal Arsenal, Woolwich. [*Received, August 21st,* 1925.]

CCCCVI.—*The Velocity of Decomposition of Heterocyclic Diazonium Salts. Part I. Diazonium Salts of the Pyrazole and Pyrazolone Series.*

By Joseph Reilly and Denis Madden.

Hitherto, so far as the authors are aware, no quantitative measurements of the stability of heterocyclic diazonium salts have been made. Qualitative examination has shown that aminopyrazole and aminopyrazolone compounds form a very distinct group, and, therefore, an investigation has been made, in the first instance, of the comparative stability of these substances under certain conditions. The

Fig. 1.



physicochemical method of Hausser and Müller (*Bull. Soc. chim.*, 1892, **7**, 721), or the modification of it devised by Cain and Nicoli (J., 1902, **81**, 1412), was found unsuitable for this particular problem, owing to the extraordinary comparative stability of some of the compounds examined, and the consequent exceptionally long period of time during which the reaction had to be followed. The process adopted by the authors was to heat a definite volume of a solution containing a known weight of the amine (sufficient to give 56 c.c. of gas at *S.T.P.*, normal diazotisation being assumed) in a specially constructed quartz vessel, A (Fig. 1), fitted with a ground stopper into which was sealed a tube passing to the bottom of the vessel. The vessel was contained in a thermostat, B, at 101·5°, which temperature was found to keep the solution of the diazonium salt at 100°, and was connected through a condenser, C, to a water-jacketed nitrometer, D. A current of air-free carbon dioxide was

periodically passed through the solution, and the liberated nitrogen was collected over concentrated aqueous potassium hydroxide.

By this method it is possible to overcome the difficulties met with by earlier investigators. The air is completely expelled from the apparatus, the vessel containing the solution is placed in the thermostat, and a current of carbon dioxide is passed through it until the temperature becomes constant (the necessary time having been determined in a control experiment); the nitrogen evolved during this time is collected and measured. It is thus possible to have an exact starting point for a solution of definite concentration. Further, no allowances such as had to be made by former investigators are necessary for the expansion of the solution and of the air in the apparatus. (The apparatus is so arranged that the air space between the surface of the solution and the mercury in the nitrometer is as small as conveniently possible.)

1-*Phenyl*-2 : 3-*dimethylpyrazolone*-4-*diazonium Chloride* (*Antipyrine*-4-*diazonium Chloride*).—A solution of 0·5075 g. of 4-aminoantipyrine in air-free water and 7·5 c.c. of *N*-hydrochloric acid (3 equivs.) was treated with 20 c.c. of aqueous sodium nitrite (1·73 g. per 200 c.c.), and the resulting solution made up to 70 c.c. The solution of the diazonium salt, originally pale yellow, developed a reddish-brown colour on warming. This evidence of a secondary reaction is supported by the fact that after 90% of the substance had decomposed the rate of gas evolution declined rapidly. The decomposition, however, was mainly a unimolecular reaction. In the table, x = the volume of nitrogen evolved after t hours (measured at 22° and 766 mm.), and $k = 1/t. \log \{a/(a - x)\}$, where a = the theoretical volume of " diazo "-nitrogen under the same conditions (= 60 c.c.).

t.	x.	$k \times 10^3$.	t.	x.	$k \times 10^3$.	t.	x.	$k \times 10^3$.
0	0·2	—	7	34·4	52·84	14½	49·6	52·50
1	8·0	62·15	8	37·5	53·20	15½	50·5	51·60
2	13·4	54·80	9	40·1	53·20	16½	51·2	50·60
3	18·2	52·32	10	42·4	53·31	17½	51·8	50·00
4	22·7	51·61	11	44·3	53·00	20½	53·0	46·00
5	27·0	51·93	12	46·1	52·93	22½	53·4	—
6	30·8	52·13	13	47·7	53·00			

Neither the addition of excess of acid nor the introduction of a small amount of colloidal gold had any marked effect on the rate of decomposition.

Antipyrine-4-*diazonium Nitrate*.—The rate of decomposition was of the same order as that of the chloride. The amount of secondary reaction was, however, slightly greater, the rate of gas evolution falling off more rapidly towards the end.

Antipyrine-4-*diazonium Sulphate*.—The rate of decomposition was

much more rapid at the beginning, and did not follow the unimolecular law, the value of k falling from 0·1305 (8 c.c. in the first ½ hour) to 0·0544 (38·8 c.c. in 9 hours); a being 57·35 c.c. That the amount of secondary reaction was considerably greater was shown by the more marked deepening of colour, and the formation of a dark reddish-brown precipitate.

The rate of decomposition, then, is in this case, considerably influenced by the nature of the anion, unlike the results obtained by Cain (*Ber.*, 1905, **38**, 2511) with benzenoid diazonium salts.

3 : 5-*Dimethylpyrazole*-4-*diazonium Chloride.*—4-Amino-3 : 5-dimethylpyrazole (0·2775 g.) was dissolved in 15 c.c. of *N*-hydrochloric acid (6 equivs.) and treated as in the foregoing cases. The amount of decomposition in 3 hours was almost inappreciable, less than 2% of the total "diazo"-nitrogen being evolved. In a second experiment, 3 equivs. of acid being used, the decomposition followed the peculiar course indicated by the following figures:

Pressure = 756 mm. Temp. = 18°. a = 60 c.c.

t	0	1	2	3	4	5	6	7
x	0·0	1·0	2·4	4·2	6·0	7·8	9·7	11·6
t	8	9	10	11	12	14	16	18
x	13·5	15·4	17·4	19·4	21·4	25·0	28·7	32·1
t	20	24	28	32	36	40	44	48
x	35·0	40·6	45·4	49·3	52·1	54·6	56·2	57·2

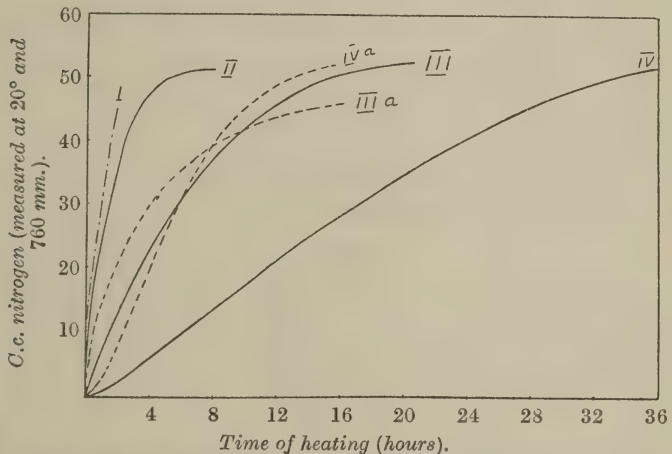
These figures show that even after 48 hours' heating the decomposition of the diazonium salt is not complete. It is evidently irregular at the beginning, less nitrogen being evolved during the first hour than during any of the subsequent 20 hours. This behaviour is probably due to the existence of two isomeric forms of the diazonium chloride, and this view is supported by the fact that when a small quantity of the base is diazotised at the ordinary temperature and added to alkaline β-naphthol, no coupling takes place for some time, whereas a colour is immediately developed if the diazonium solution has previously been boiled for a few minutes. After the fourth hour, the decomposition proceeds with some degree of regularity, but not in accordance with the unimolecular law.

3 : 5-*Dimethylpyrazole*-4-*diazonium Sulphate.*—As in the case of the chloride, the reaction was irregular at the beginning. From the end of the fourth hour to the end of the twelfth hour the rate of decomposition followed the unimolecular law, the mean value of k being 0·0720. A solution of the diazonium salt containing an excess of sulphuric acid (6 equivs.) was remarkably stable, only 2% of the total "diazo"-nitrogen being evolved in 3 hours.

Pyrazole-4-*diazonium Chloride.*—3 : 5-Dimethylpyrazole was converted by Knorr's method (*Annalen*, 1894, **279**, 218) into the corre-

sponding 3 : 5-dicarboxylic acid, the latter, however, being isolated from the oxidation product by the addition of hydrochloric acid without the intermediate formation of the acid potassium salt. Pyrazole, obtained by heating the dry dicarboxylic acid at 270—275°, was converted by Buchner and Fritsch's method (*Annalen*, 1893, **273**, 265) into the 4-nitro-compound. This was isolated by adding ice to the nitration mixture, and was reduced as follows: A solution of 3 g. of the nitropyrazole in 100 c.c. of moist ether was treated, with cooling, with a large excess of an aluminium–mercury couple during a few hours, complete reduction being indicated by

FIG. 2.



I o-*Nitrobenzenediazonium chloride.* II *Pyrazole-4-diazonium chloride.* III 1-*Phenyl*-2 : 3-*dimethylpyrazolone*-4-*diazonium chloride.* III*a* 1-*Phenyl*-2 : 3-*dimethylpyrazolone*-4-*diazonium sulphate.* IV 2 : 3-*Dimethylpyrazole*-4-*diazonium chloride.* IV*a* 2 : 3-*Dimethylpyrazole*-4-*diazonium sulphate.*

the disappearance of the purple colour initially developed. The ether was distilled off, the residue extracted a few times with boiling alcohol, air being excluded, and the extract was immediately treated with hydrochloric acid. The product was evaporated, and the residue recrystallised from alcohol; 4-aminopyrazole dihydrochloride then separated. As the quantity obtained was small, the somewhat dark product was not further purified before diazotisation.

The rate of decomposition of the diazonium chloride from 0·39 g. of the dihydrochloride approximately obeyed the unimolecular law. In 5 hours, 83% of the total "diazo"-nitrogen was evolved, but thereafter the rate of decomposition declined very rapidly. The much more rapid decomposition of this substance seems to indicate

that the methyl groups in diazotised 3 : 5-dimethylaminopyrazole have a stabilising influence on that diazonium salt.

The comparative stability of the diazonium chlorides from 4-aminoantipyrine, 4-amino-3 : 5-dimethylpyrazole, and 4-aminopyrazole may be judged from the curves in Fig. 2, showing the rate of gas evolution at various intervals.

Of the large number of benzenoid diazonium salts investigated by Cain and Nicoll (*loc. cit.*) the most stable (and the only two apparently sufficiently stable for examination at 100°) were those from *o*- and *m*-nitroaniline. The conditions under which the experiments described above were carried out were different from those employed by earlier investigators, but results closely analogous to those of Cain and Nicoll were obtained in a control experiment in which *o*-nitroaniline was used. A comparison of the results obtained from the diazonium chlorides in the pyrazole and pyrazolone series with those from *o*- and *m*-nitroaniline is therefore justifiable (for 4-amino-3 : 5-dimethylpyrazole, the results are the mean of the experiments in which only 3 equivalents of hydrochloric acid were used in the diazotisation).

Substance.	k (t measured in mins.).	% Decomp. in first hr.	Time (mins.) for half decomposition.
m-Nitroaniline	0·0332	100	10
o-Nitroaniline	0·00564	54	53
4-Aminopyrazole	0·00317	40	80
4-Aminoantipyrine	0·00088	13	360
4-Amino-3 : 5-dimethylpyrazole	0·00030	1·7—2	1020

In the case of 4-amino-3 : 5-dimethylpyrazole the rate of decomposition of the diazonium chloride was considerably slower (3 to 4 times) when excess of acid (6 equivs.) was employed. It cannot be said, as of benzenoid salts, that the rate of decomposition in the case of heterocyclic diazonium salts is uninfluenced by the nature of the anion, for the diazonium sulphates of both 4-aminoantipyrine and 4-amino-3 : 5-dimethylpyrazole decomposed much more rapidly than the corresponding chlorides.

University College, Cork. [*Received, September 7th,* 1925.]

CCCCVII.—*The Swelling and Dispersion of Some Colloidal Substances in Ether–Alcohol Mixtures.*

By Ernest Walter John Mardles.

It is well known that cellulose nitrate and Kauri copal each dissolve readily in a mixture of ethyl alcohol and ethyl ether, although the liquids taken singly are non-solvents, and that the solubility of

potassium stearate, sandarac resin, or night-blue in such a mixture is greater than the mean value of the solubilities in either constituent. This characteristic solvent action appears to be general with a large number of colloidal substances and mixtures of liquids, *e.g.*, gelatin in water–acetic acid, potassium oleate in alcohol–water, casein in pyridine–water, but no satisfactory explanation of it appears yet to have been made. Baker's view that in ether–alcohol mixtures the intrinsic solvent for cellulose nitrate is a loose molecular complex of alcohol and ether (J., 1912, **101**, 1409) has been considerably criticised (Report of Discussion on Colloids held jointly by the Faraday and Physical Societies, 1920). Barr and Bircumshaw have proposed the hypothesis, previously rejected by Baker, that the " best solvent " of cellulose nitrate is unimolecular alcohol.

A close study of the phenomena, in particular the gelation of the sols and swelling behaviour, indicates that a complete explanation must involve the significant fact that swelling precedes dispersion. The important bearing that swelling has on peptisation or dispersion in mixed liquids was recognised many years ago by Tompkins (*op. cit.*, appendix 2), but his view that dispersion is an extreme case of what in lesser degree is known as swelling is now regarded as erroneous.

It appears that the ether in an ether–alcohol mixture not only acts as a diluent, disturbing the equilibrium $(R{\cdot}OH)_n \rightleftharpoons nR{\cdot}OH$, but also actually enters the complex which the molecules of the dispersion medium form with the colloid.* Baker pointed out that when the ether is replaced by another non-solvent there is not necessarily formed a solvent mixture for cellulose nitrate. Although he was probably right in ascribing to the ether an active part in the solvent action, yet his hypothesis as to the particular mode of action is not in accord with fact.

It has been found as a general principle that the characteristic solvent action of mixed liquids cannot be ascribed to the intrinsic action of one kind of molecule or molecular complex, but whenever molecular simplification occurs in a liquid mixture there is increased solvent action. Therefore, when compound formation occurs between the components of a binary mixture, loss of solvent power is to be expected. Indeed, it is possible to use a colloidal substance, *e.g.*, cellulose acetate, to detect the presence of a molecular compound in a system of liquids (Mardles, J., 1924, **125**, 2244).

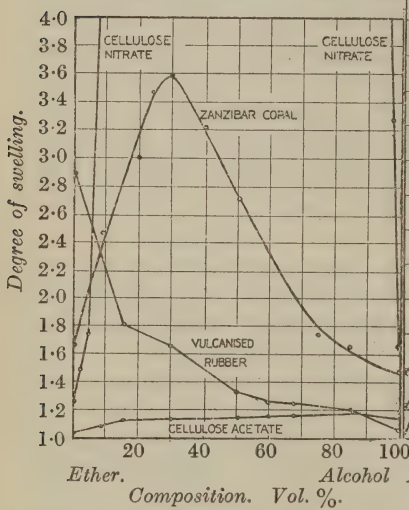
The action of mixed liquids on colloids presents a number of striking features both with regard to swelling and to peptisation. If cellulose nitrate be soaked in dry ether or absolute alcohol, there

* Kugelmass (*Rec. trav. chim.*, 1922, **41**, 751) has shown that ether favours the peptisation of cellulose dinitrate, and alcohol that of the trinitrate.

is little apparent change even if the temperature be varied from − 80° to + 100°, but a certain amount of swelling occurs. With the addition of the second liquid there is a rapid increase in the degree of swelling. For example, a film of cellulose nitrate, after immersion at the ordinary temperature for a few days, increased 28% in weight in dry ether and 68% in absolute alcohol; in ether containing 5% (vol.) of alcohol the increase was 75%, and any

FIG. 1.

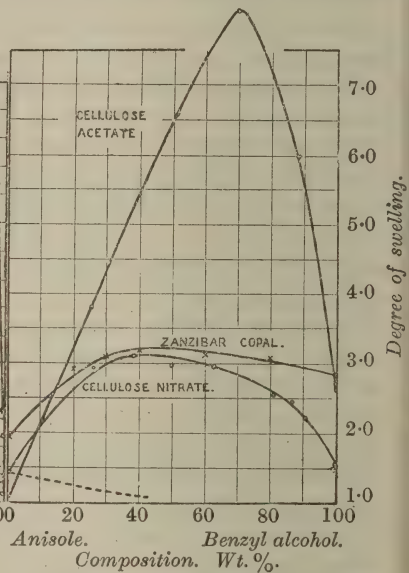
The swelling of some colloidal substances in mixtures of ethyl alcohol and ethyl ether at 18° *after* 7 *days' immersion.*



About 10–15% *of the copal dissolved. The values for this substance refer to the undissolved portion and were obtained by determining the amount of resin in the swollen clot.*

FIG. 3.

The swelling of some colloidal substances in mixtures of anisole and benzyl alcohol.



The chained line indicates the swelling of cellulose nitrate in a mixture of anisole and phenol.

further addition of alcohol resulted in a very high degree of swelling. Similarly, the addition of 2·5% of ether to alcohol increased the swelling to such an extent that less than one-third of the swollen mass was cellulose nitrate and dispersion of the more soluble constituents began.*

In Fig. 1 are shown the degrees of swelling, in ether–alcohol mixtures, of (*a*) cellulose nitrate, (*b*) Zanzibar copal, (*c*) vulcanised

* The cellulose esters, like cellulose, and other colloidal substances, *e.g.*, the resins, are heterogeneous and it is possible to separate them into fractions of different solubility and viscosity.

rubber, and (*d*) cellulose acetate. The degree of swelling is expressed as the weight of the swollen mass obtained from 1 gram of the dry colloid.

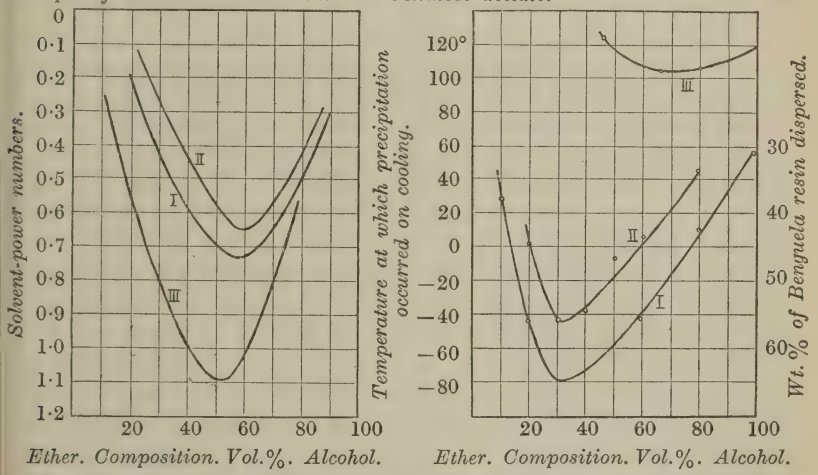
Materials.—The ether was dried over sodium and fractionated. Absolute alcohol was used. The cellulose nitrate (N, 10·7%) was obtained in film form by leaving an acetone solution to evaporate slowly in a flat dish. The film was thoroughly dried by leaving it in the air for several months. About 0·5 g. of the film was

FIG. 2.

The solvent power of ethyl alcohol–ethyl ether mixtures for cellulose nitrate, Kauri gum, etc.

Cellulose nitrate.
I, *Nitrogen content*, 10·7%. II, *Nitrogen content*, 11·5%. III, *Approximately 5% of water present in the solvent mixtures, and another sample of cellulose nitrate used.*

I, *Kauri copal.* II, *Benguela copal.* III, *Cellulose acetate.*



The solvent-power numbers were obtained by noting the relative quantities of a diluent, e.g., *hexane, required to be added to* 1 *c.c. of the sol* (*concentration* 5/100; *temperature* 20°) *in order to start precipitation of the colloid.*

immersed in about 20 c.c. of the liquid. The Zanzibar copal used was from the same sample throughout, and the vulcanised rubber consisted of ordinary black rubber tubing extracted with acetone. The cellulose acetate (Rhône) had an acetyl content of 39·6%, corresponding with the formula $C_{12}H_{15}O_5(O{\cdot}CO{\cdot}CH_3)_5$.

The swelling results obtained for cellulose nitrate when dispersion did not occur seem to indicate that the degree of swelling in ether–alcohol mixtures tends to increase enormously with further additions of the second liquid. The experiments of Masson, who found that fibrous cellulose nitrate absorbed a maximum amount of

ether–alcohol vapour when this was composed of 1 mol. of ether and 1 mol. of alcohol, apparently support this view (*op. cit.*, p. 95).

It is significant that the optimum solvent mixture of alcohol and ether for cellulose nitrate has an equimolecular composition only when a little water is present. It contains more alcohol if the materials have been carefully dried (compare Stepanow, *Z. ges. Schiess-u. Sprengstoffw.*, 1907, **2**, 43; Matteoschat, *ibid.*, 1914, **9**, 105).

The close relationship between the degree of swelling and solvent action is shown clearly in the case of the copal resins. Zanzibar copal, one of the harder and more intractable copals, swells considerably in ether–alcohol mixtures, but the amount of dispersion is small. On the other hand, the softer Kauri resin dissolves in the mixtures and, on cooling sufficiently, either the solution gelates or the resin is precipitated as an amorphous mass. With Benguela copal of intermediate hardness, a part of the resin is dispersed and the remainder swells considerably. The optimum solvent mixture, *i.e.*, the one which dissolves the resins most readily, forming solutions that are most stable against precipitation by cooling or addition of diluents, has practically the same composition as the mixture of liquids in which maximum swelling occurs in the case of the harder copals. The degree of swelling of Zanzibar copal reaches a maximum when the proportion of ether is 70% by volume (Fig. 1), and this mixture exerts the maximum solvent action on Kauri and Benguela copal (Fig. 2).

The very marked influence of swelling on dispersion is also shown by the study of the binary mixture anisole–benzyl alcohol. Cellulose nitrate is swollen but not dispersed by this mixture, and it is possible to plot the whole of the swelling curve. The swelling of cellulose acetate is considerable and dispersion occurs on warming, so it is possible to note the relation between degree of swelling and solvent action. Towards the copals, this binary mixture behaves as the previous one (Table I and Fig. 3).

The anisole used had d_4^{25} 0·989 and b. p. 155°. Of the benzyl alcohol, $d^{25°}$ 1·043, 95% distilled between 205° and 206°.

It is seen from Table I that the swelling of cellulose nitrate continues in anisole during the 31 days, but becomes constant in some of the mixtures after 15 days. This fact, that the rate of swelling is highest when the swelling is greatest, is of importance in explaining why the " best " solvent mixture disperses the most rapidly; for not only does the optimum solvent mixture often form the least viscous sol, so that the resistance to the diffusion of the colloidal particles from the surface during dispersion is at a minimum, but also the initial swelling of the colloid is most rapid.

Table I.

The swelling action of mixtures of benzyl alcohol and anisole at 18°. *a* denotes the wt.% of anisole in the mixture, and *b* the degree of swelling.

Cellulose nitrate.

a	100	74	62·2	50	37·5	28	19·2
b after 7 days	1·25	1·75	3·06	2·0	2·12	2·13	—
„ 15 „	1·35	2·80	3·22	2·90	2·98	2·83	1·5
„ 21 „	1·42	2·87	3·22	2·90	2·98	2·85	2·1
„ 31 „	1·47	2·92	3·22	2·90	2·98	—	2·55

a	13·7	9·6	0
b after 7 days	1·37	—	1·11
„ 15 „	1·80	1·85	1·27
„ 21 „	2·25	2·2	1·4
„ 31 „	2·5	2·4	1·56

Zanzibar copal.

a	100	80	70	60	40	20	0
b after 2 days	1·45	2·1	1·9	2·2	2·0	2·2	2·1
„ 5 „	1·93	2·9	3·1	3·2	3·1	3·1	2·8
„ 27 „ *.....	2·0	4·1	4·2				

(i) *Cellulose acetate* and (ii) *Gelatin* (Coignet's).

a	100	75	47·5	30	12	0
b after 5 days (i) ...	1·09	3·85	6·6	8·2	6·0	2·6
„ „ (ii) ...	1·06	1·05	1·00	1·00	1·03	1·07

* By this time the resin was very soft and tacky and very difficult to manipulate.

The swelling of cellulose acetate is at the maximum in the benzyl alcohol–anisole mixture containing 50% of anisole, and Table II shows that this is also the optimum solvent mixture. Similarly, the composition of the best solvent mixture for Kauri copal is practically that of the mixture in which Zanzibar copal swells the most. Air-dried cellulose acetate dissolved in benzyl alcohol on warming. On cooling rapidly, a 5% sol became turbid at 18° owing to separation of the acetate. The temperature of separation was first lowered and then raised on addition of anisole.

Table II.

The solvent action of mixtures of benzyl alcohol and anisole on cellulose acetate and Kauri copal.

w = wt.% of anisole and t = temperature of precipitation or gelation.

Cellulose acetate.

w	0	12	26	40	54	66	72	78
t	18°	10°	5°	4°	12°	38°	65°	90°

Kauri copal.

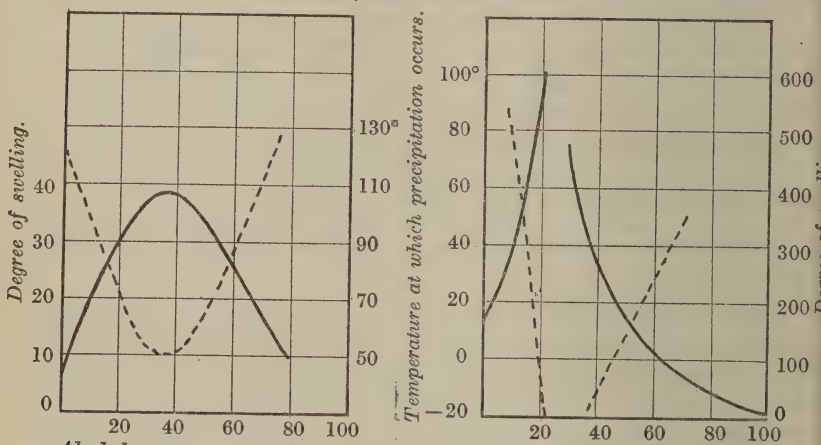
w	100	90	75	60	40	20	0
t	90°	33°	−25°	−60°	−52°	−42°	−22°

The Kauri copal dissolved in anisole on warming, but separated when the temperature fell below 90°. The addition of benzyl alcohol facilitated the dispersing action and the solutions were stable at lower temperatures.

The important influence of swelling on dispersion can be shown equally well with other binary mixtures, *e.g.*, alcohol and water. Knoevenagel and his co-workers (*Koll. Chem. Beiheft*, 1921, 1922, 1923) have measured the swelling of cellulose acetate in a number of binary mixtures, and the solvent action of many of these mixtures on the same substance has been determined (Mardles, *J. Soc.*

FIG. 4.

The correlation of the swelling of cellulose acetate in binary mixtures (Knoevenagel) with solvent action.



—— *Degree of swelling (Knoevenagel); --- Temperature of precipitation (Mardles,* loc. cit.).

Chem. Ind., 1923, **42**, 127). There is a close correlation in most cases, although different varieties of cellulose acetate were used.

Gelatin and vulcanised rubber differ from the cellulose esters and the resins in that their degree of swelling in ether–alcohol mixtures is less than the mean value.

The swelling of cellulose nitrate in phenol–anisole is quite different from that in benzyl alcohol–anisole, there being no maximum to the curve.

TABLE III.

The swelling of cellulose nitrate in phenol–anisole mixtures.

Wt. % of phenol	0	10	27·5	44
Degree of swelling	1·47	1·39	1·21	1·07

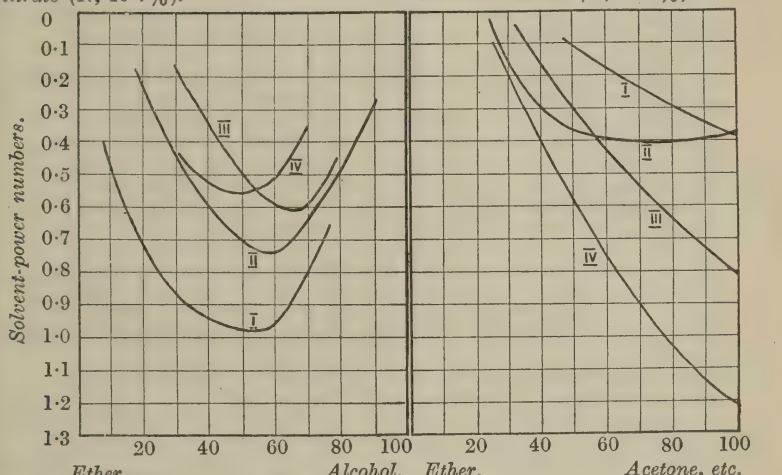
A parallel behaviour is found in the dispersion process, for, if either ether or alcohol be replaced by another liquid, the characteristic solvent action of the ether–alcohol mixture is not necessarily repeated. The solvent power of various binary mixtures containing ether for the sample of cellulose nitrate used is shown in Fig. 5. The solvent power numbers were obtained in the manner already described (J., 1924, **125**, 2244).

The explanation of the characteristic dispersing action of mixed liquids must be sought in the cause of the increased swelling, and,

FIG. 5.

The solvent action of various binary mixtures of ethers and alcohols on cellulose nitrate (N, 10·7%).

The solvent action of various binary mixtures containing ethyl ether on cellulose nitrate (N, 10·7%).



I, *Benzyl methyl ether and ethyl alcohol.* II, *Ethyl ether and ethyl alcohol.* III, *Ethyl ether and benzyl alcohol.* IV, *Anisole and ethyl alcohol.*

I, *Ethyl ether and epichlorohydrin.* II, *Ethyl ether and acetic acid.* III, *Ethyl ether and acetone.* IV, *Ethyl ether and ethyl acetate.*

from the cases examined, the specific characters of the liquids and colloidal substances are evidently of primary importance. Cellulose nitrate in an ether–alcohol mixture probably attaches to its particles both kinds of molecules from the dispersion medium, and these attracted molecules may bind additional ones.

Esselen (*J. Ind. Eng. Chem.*, 1920, **12**, 801), discussing the characteristic solvent action of mixtures of chloroform and alcohol on cellulose acetate, puts forward a possible explanation based on the fact that cellulose and its compounds have marked affinities for the hydroxyl group of alcohol. Mixtures of liquids containing as one constituent a substance with reactive groups, such as an alcohol, ketone, or acid, especially if this constituent is the first

member of a homologous series, usually have markedly high solvent action. A liquid, such as hexane or xylene, which is not particularly reactive and is a high member of a homologous series behaves like a diluent or inert component in a binary mixture.

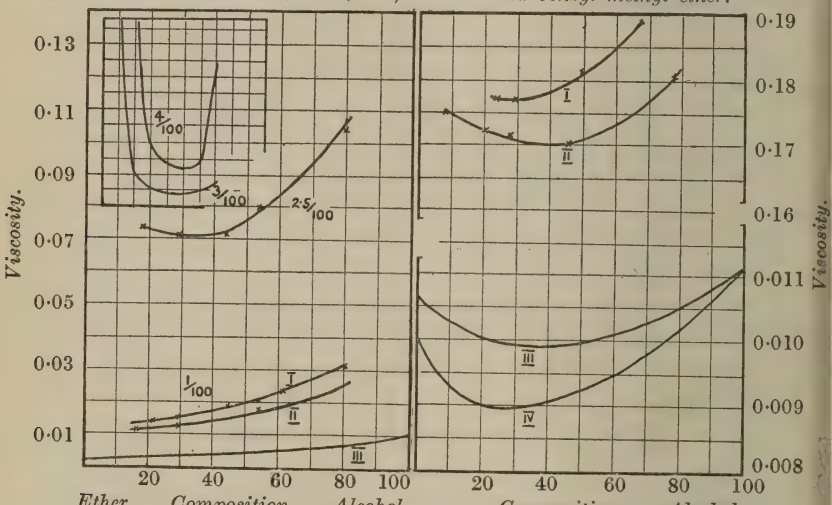
The structure of the complex formed by the molecules of the dispersion medium and a colloidal particle is apparently simple, for the composition of the best solvent mixture is often simple, molecularly (Mardles, J., 1924, **125**, 2244), and Knoevenagel has

FIG. 6.

The viscosity of solutions of cellulose nitrate in ether–alcohol mixtures.

Mixtures of ethyl alcohol and ethyl ether.
Inset: Viscosity results of Gibson and McCall (J. Soc. Chem. Ind., 1920, 172).

Mixtures of ethyl alcohol with anisole and benzyl methyl ether.



I, *Cellulose nitrate*, 11·5% N. II, *Cellulose nitrate*, 10·7% N. III, *Pure liquids.*

I, 2·5/100 *in anisole–ethyl alcohol.* II, 2·5/100 *in benzyl methyl ether–ethyl alcohol.* III, *Benzyl methyl ether–ethyl alcohol.* IV, *Anisole–ethyl alcohol.*

shown, in the case of the swelling of cellulose acetate in mixed liquids, that the proportion of the constituents in the swollen mass is often a simple molecular one also.

Viscosity and Density of the Sols.—The effect of the addition of a colloidal substance on the viscosity of a binary mixture of liquids is, in general, such that the shape of the viscosity–composition curve becomes exaggerated and any special feature of it is developed (Mardles, J., 1924, **125**, 2244). These effects are produced when cellulose nitrate is added to ether–alcohol mixtures (Table IV and Fig. 6). The sag in the viscosity curve for the pure liquids is exaggerated and, for the sols of higher concentration, there is a minimum

point, which occurs at a composition near that of the optimum solvent mixture.

TABLE IV.

The viscosity and density of sols of cellulose nitrate in mixtures of ethyl alcohol and ethyl ether.

Concentration of sol, 1/100. Nitrogen content of nitrate: a, 10·7%; b, 11·5%.

Wt. % of ether.	Difference in density between dispersion medium and sol.		Viscosity.	
	a.	b.	a.	b.
20·0	0·0045	0·0060	0·026	0·031
38·4	—	0·0074	—	0·024
47·2	0·0085	0·0077	0·019	0·021
56·7	—	0·0075	—	0·019
70·6	0·0078	0·0076	0·0136	0·015
78·0	—	0·0056	—	0·014
84·2	0·0065	0·0059	0·011	0·014

Concentration, 2·5/100. Nitrogen content, 10·7%.

20·0	0·0135	0·105
47·2	0·0174	0·080
56·7	0·016	0·072
71·6	0·013	0·072
84·2	0·014	0·074

TABLE V.

The viscosity and density of sols of cellulose nitrate in mixtures of benzyl methyl ether and ethyl alcohol.

Benzyl methyl ether, b. p. range 167—169°, $d^{25°}$ 0·963.

Wt. % of benzyl methyl ether.	Density.		Viscosity.	
	Liquids.	Sol, 2·5/100.	Liquids.	Sol, 2·5/100.
100	0·963	—	0·0107	—
92	0·9465	0·955	0·0104	0·175
78·9	0·932	0·9434	0·01001	0·1726
72·8	0·9189	0·9311	0·01007	0·172
55·3	0·8863	0·8983	0·01002	0·170
26·4	0·8322	—	0·01036	—
22	—	0·8455	—	0·181

The viscosity and density of sols of cellulose nitrate in mixtures of anisole and ethyl alcohol.

Wt. % of anisole.	Density difference.	Viscosity of sol, 2·5/100.
77·1	0·0113	0·1772
71·6	0·0116	0·177
51	0·0118	0·184
31·9	0·0115	0·189

From the differences in density between the dispersion medium and the sols it will be seen that the greatest volume changes occur when the compositions of the mixed liquids are near that corresponding to the maximum sag in the viscosity curve and when the solvent power of the mixed liquids is high (Fig. 5).

Surface-tension Measurements.—A large number of measurements of the surface tensions of the organosols in ether–alcohol mixtures and in the single liquids were made at different temperatures and for different concentrations by means of Sugden's maximum bubble pressure method (J., 1924, **125**, 27). In the case of ethyl alcohol and its mixtures with ethyl ether, benzyl methyl ether, and anisole, the effect of the addition of the colloidal substance was to *raise* the surface tension of the dispersion medium. Similarly, the ether organosols had higher surface tensions than the pure liquids.

The temperature coefficient of the surface tension from 10° to 30° for the organosols was practically the same as that for the pure dispersion medium.

Tables VI and VII give a selection of the results obtained.

TABLE VI.

Ethyl ether sols of concentration 1/100.	$\gamma^{25°}$ in dynes/cm.	Ethyl alcohol sols.	γ in dynes/cm.
(Ethyl ether).	16·6	(Ethyl alcohol).	21·7 at 28°
Chlorophyll.	16·65	Potassium oleate, 0·25/100.	22·1 ,,
Tung oil.	16·6	,, ,, 0·5/100.	22·3 ,,
Copper oleate.	16·8	(Ethyl alcohol).	21·9 at 25°
Mastic (5/100).	16·85	Tannic acid, 2/100.	22·1 ,,
Dragon's blood.	16·8	,, ,, 10/100.	22·7 ,,

The surface tension of ethyl alcohol was also raised slightly by the addition of shellac, night-blue, and potassium stearate, but no appreciable effect was produced by sandarac resin and chlorophyll.

TABLE VII.

The surface tension of some sols in ethyl ether–ethyl alcohol mixtures at 25°.

Wt. % of ether.	γ for the liquid.	Sols.	γ.
63·9	18·6	Cellulose nitrate, 5/100.	20·1
		,, ,, 2/100.	19·7
		Chlorophyll.	18·8
		Dragon's blood, 2/100.	19·6
		Copper oleate, 2/100.	19·6
33·1	19·6	Cellulose nitrate, 5/100.	21·4
		,, ,, 2/100.	20·1
		Chlorophyll, 2/100.	19·9
		Copper oleate, 2/100.	20·0
		Tannic acid, 2/100.	20·1
13·1	20·9	Chlorophyll, 2/100.	20·95
		Kauri resin, 5/100.	21·2

Chlorophyll had practically no effect on the surface tension of binary mixtures of alcohol with anisole or benzyl methyl ether, but cellulose nitrate raised it a little.

TABLE VIII.

Composition.	$\gamma^{25°}$ for the liquid.	Sols.	$\gamma^{25°}$.
Anisole, 71·6%.	27·7	Cellulose nitrate.	28·3
Benzyl methyl ether, 44%.	26·8	Night blue.	27·2
		Cellulose nitrate.	28·3
,, ,, 26·4%.	24·0	,, ,,	25·2
		Dragon's blood.	24·5

The surface tension of a mixture of 2 vols. of benzyl alcohol and 1 vol. of anisole at 20° was raised from 37·3 to 38·2 by cellulose acetate (2/100), and slightly by night-blue.

Summary.

A study has been made of the swelling and the dispersion action of ether–alcohol mixtures on colloidal substances. The explanation of the high dispersing action of the mixed liquids must be sought in the cause of the colloidal substances swelling initially to a greater extent in the mixtures than in the liquids taken singly, there being a close correlation between the swelling and the dispersing action.

The attraction between a colloidal particle and the molecules of the mixed dispersion medium, due to the presence of mutually reactive groups, whereby complexes are formed, appears to reach a maximum with certain combinations of liquids because of the special spatial arrangement and interlocking of the various molecules in the complex resulting from their size, from the relative strengths of their affinity bonds, etc., so that it is necessary in any explanation to consider the relative specific characters of the liquids and the colloidal substance.

With increase in the solvent power of the liquid mixtures for cellulose nitrate, the change in density increases and the sols become relatively less viscous.

The surface tensions of the organosols are either the same as or slightly higher than that of the pure dispersion medium.

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CCCCVIII.—*The Allotropy of Zinc.*

By DAVID STOCKDALE.

THE work here described was undertaken in order to discover some sure means of recognising allotropy in metals at high temperatures and of accurately determining those temperatures. The experiments of other workers, those in which *X*-rays were used being left out of account, may be divided into two groups :

(*a*) Investigations of the physical properties of the metal, quenched from temperatures above and below that of the suspected transformation point.

(*b*) Experiments carried out in the neighbourhood of the transition point.

Objection to the former experiments can be made on three grounds :

(1) There is no certainty that, during the quenching, an allotropic metal does not revert to its original form.

(2) During the chilling of even a small specimen very great stresses are created, and these may cause false results to be obtained.

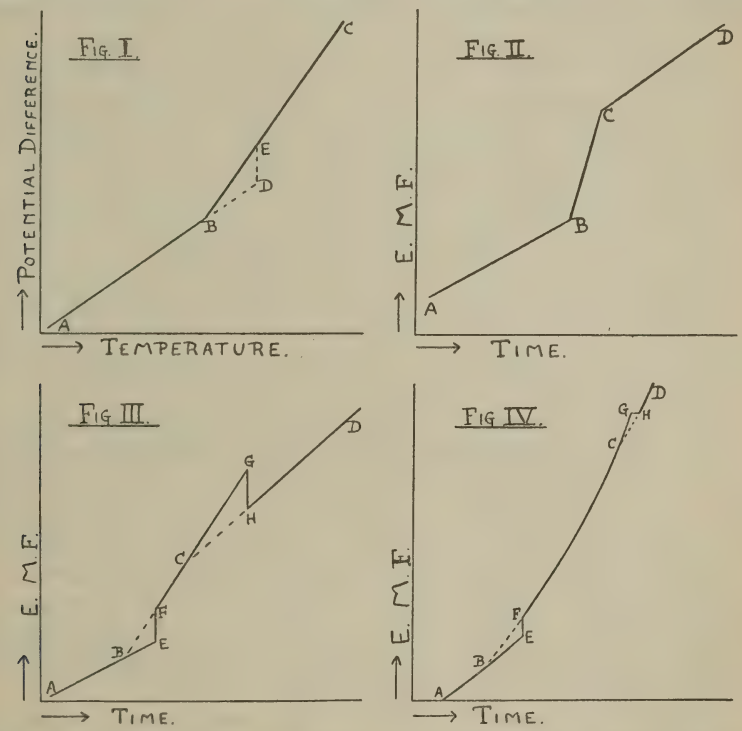
(3) Very little is known about the phenomena of " lag " in allotropic changes at high temperatures. It is possible that this lag may be so great that the temperature may be raised considerably above that of the transformation without any change taking place in the metal.

The third criticism can be made of the latter group of experiments also, which have consisted, for example, in investigations into the specific heats of metals at high temperatures, measurements of electrical resistance, of thermal electric power, and of the mechanical properties of the materials, but the most serious objection is that these methods are not infallible. For example, it has been shown by Miss Bingham (*J. Inst. Metals*, 1920, **24**, 333)—and confirmed by the author—that zinc undergoes an allotropic change between 310° and 330° ; yet of all the physical properties of zinc, only the electrical resistance and the " mechanical " properties are definitely discontinuous through that range of temperature. Miss Bingham has shown that in the case of zinc the change in resistance is extremely small in comparison with the resistance. Attempts to carry out exact measurements with an ordinary tensile testing-machine would probably be futile.

The problem to be solved was to devise some method of measuring the change in a property of a metal in such a way that this change would appear large with respect to the quantity measured just prior to the transformation.

There is between a metal and an electrolyte in contact with it a certain difference of potential, which is a function of the temperature. If the potential difference and the temperature be plotted, the result may be a curve similar to A B (Fig. I). At the triple point (α-allotrope, β-allotrope, vapour) the solution pressure of the two forms must be the same, and therefore, if B represents the triple point, B must also lie on the potential difference–temperature curve (B C) of the β-allotrope. But there seems to be no reason why the slope of A B and of B C should be the same, and if exact measurements of

differences of potential could be made, triple points of metals which exhibit allotropy could probably be detected by changes in direction of the curve. The effect would be increased by "lag"; that is to say, one form might exist in a metastable condition over a range of temperatures and then suddenly change into the other. If such were the case, the curve would be of the form A B D E C and the triple point would be found by producing C E until it cut A D. By the use of this principle, Cohen (*Z. physikal. Chem.*, 1894, **14**, 53; see also Roozeboom, "Die Heterogenen Gleichgewichte vom Stand-



punkte der Phasenlehre," Vol. I, p. 123) was able to measure accurately the transition temperature of tin.

If a second electrode of the metal is immersed in the electrolyte, and connected with the first, a small, constant difference of temperature being maintained between them, an electrolytic cell will be formed having a very small *E.M.F.* The *E.M.F.*–temperature (or time) curve will be the algebraical difference between two curves such as A B C (Fig. I), and should have the form A B C D (Fig. II), B and C representing the temperatures at which the allotropic change takes place in the two electrodes. If allowance is made for

"lag," the theoretical curve should be of the form A B E F C G H D (Fig. III), and by producing the lines G F and D H the triple point should be ascertainable. The order of magnitude of the *E.M.F.* and of the changes in it can be made the same by choosing a suitable temperature difference between the two electrodes.

Experimental.

As it appeared certain, from the work of Miss Bingham, that zinc undergoes allotropic change at about 300°, it was thought advisable to test the foregoing theoretical conclusions by carrying out experiments with that metal before seeking such changes in others.

The zinc used was "Brunner Mond's purest electrolytic." The choice of an electrolyte was limited, because the liquid must not attack the zinc in any way, either by oxidation or by deposition of a second metal on it, and preliminary experiments had indicated that no gas must be given off when the electrolyte is heated. Finally, a mixture of zinc chloride, containing much oxychloride, with 10% of zinc bromide, was used. It melted at about 280°.

The apparatus consisted of a hard glass U-tube, 1·5 cm. in diameter, the limbs being 4 cm. apart and 22 cm. long. One limb was wound with nichrome ribbon protected from oxidation by pyruma cement, and could be heated by passing a small current through the ribbon.

The U-tube was placed in an electrical resistance furnace so that the limbs projected a distance of 5 cm.; the empty portion of the furnace was lightly packed with asbestos fibre. The quantity of electrolyte was such that the level of the molten material was 6 cm. above the bottom of the tube. To stop convection currents, the connecting piece was lightly plugged with glass wool.

The difficulty arising through the molten zinc salts running up the hot tube and solidifying near the top was overcome by winding the tops of both limbs with nichrome ribbon and keeping them considerably hotter than the bottom parts.

The zinc electrodes, 0·4 × 0·4 × 6 cm., were attached to stout copper wires passing through the rubber stoppers closing the limbs. The stoppers were also fitted with rubber valves, preventing access of atmospheric moisture. The copper wires were connected through a mirror galvanometer. In the circuit were a reversing key and an apparatus for opposing an *E.M.F.* to that generated by the little cell. The galvanometer threw a spot of light on a sheet of paper moving upwards at a uniform rate, and by following the spot of light with a pencil it was possible to draw an *E.M.F.*–time curve in a direct and easy way.

Temperatures were measured by copper–constantan couples

(size 30 gauge) sheathed in fine glass tubes, and so placed that the hot junctions were about 1 cm. above the bottoms of the electrodes. The couples were used in conjunction with millivoltmeters, standardised by means of the melting points of pure zinc, lead and tin.

Before a series of experiments was begun, the U-tube and its contents were heated to 400° to drive off any steam and to anneal the zinc. The tube was then heated or cooled at different rates through the range where the allotropic change might be expected to occur, the two limbs being kept at slightly different temperatures, and *E.M.F.*–time curves were drawn. An attempt was made to read the millivoltmetres every other minute.

The apparatus described above is unsatisfactory and the experimental difficulties are numerous. First, a single operator has too much to do if he is to obtain correct results. Then there are troubles with the electrolyte. It was found impossible to maintain a uniform temperature difference between the two limbs, and consequently the curves obtained were not sharp. As the galvanometer was not sufficiently sensitive, the breaks in the curves were very small, and were liable to be completely obscured by small experimental errors.

Sixteen curves in all were taken. The results obtained from eight of the more convincing experiments are in the following table : t is the time (mins.) taken for the temperature to change from 300° to 330°, and T the difference in temperature of the electrodes.

Type of curve.	T.	t.	E.	B.	G.	C.
Cooling.	6°	35	316°	318°	314°	316°
,,	15	30	—	—	308	—
,,	12	26	312	314	314	—
,,	7	Not obs.	312	314	308	313
Heating.	10	35	315	313	317	315
,,	6	30	316	—	315	315
,,	10	18	—	—	318	—
,,	10	7	328	—	318	—
			Mean	315		315

The letters above the columns refer to Fig. III. Blanks in the columns denote either that the position of the break was very doubtful or that the curve was of such a shape that it was impossible to find the point B or C accurately by interpolation.

Experiment 8, in which the rate of heating was fast, is interesting in that the lag in the hotter electrode was so great that the point F (Fig. III) lay between the points C and G, and the line F G was very short because the cooler electrode underwent the transformation almost immediately after the other.

The figures in columns B and C show that there is a transition point at 315°. It will be seen, also, that there is a "lag" at the rates of heating employed, but in no case was the measured "lag" very great. The largest values obtained were 7° below the mean temperature on cooling curves, and 13° above the mean temperature on heating curves. It is quite possible that this phenomenon of "lag" may have been responsible for the many failures to obtain breaks in the curves.

Fig. IV is an exact reproduction of the curve obtained in Experiment 4. In general, the others resembled it; in many cases, however, the observed breaks were much larger and sometimes they were not nearly so regular in shape.

Conclusion.

The experiments indicate that zinc undergoes allotropic change at 315°. This result agrees very well with those of Miss Bingham (*loc. cit.*), who found that changes occurred in some properties of zinc at about 330° and in others at about 310°.

The figures set out in the table seem convincing; the curves from which these figures are derived are not convincing, and the value 315° is to be accepted only with reserve.

The author regrets that circumstances have arisen which make it impossible for him to continue this work. His conviction that the principle underlying his experiments is correct and that a further attempt to apply it both to the examination of zinc and of other metals will yield valuable results, is his excuse for offering this paper for publication. In his opinion it is necessary to provide some means of confirming the existence of allotropic changes revealed by the use of *X*-rays.

The author expresses his gratitude to Mr. C. T. Heycock, M.A., F.R.S., for his interest and help, and to the Royal Commissioners of the Exhibition of 1851 for a senior studentship.

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UNIVERSITY OF CAMBRIDGE. [*Received, August 10th,* 1925.]

CCCCIX.—*Electrometric Study of the Reactions between Alkalis and Silver Nitrate Solutions.*

By HUBERT THOMAS STANLEY BRITTON.

PRECIPITATES formed by the addition of alkalis to metallic salt solutions are, as a rule, basic. Silver oxide, however, appears to be an exception and therefore its precipitation by sodium hydroxide has been studied.

The precipitation of silver oxide from silver nitrate solution by ammonia and its subsequent re-solution have been studied from various points of view. Prescott (*Chem. News*, 1880, **42**, 31), Reychler (*Ber.*, 1883, **16**, 990), Draper (*Pharm. J.*, 1886, **17**, 488), and Herz (*Z. anorg. Chem.*, 1910, **67**, 248) found that when approximately 2 mols. of ammonia were added to 1 mol. of silver nitrate the precipitate formed redissolved. That the substances in these proportions do enter into some kind of reaction has been shown by the following physicochemical methods: cryoscopy and conductivity (Reychler, *Ber.*, 1883, **16**, 2421; 1895, **28**, 555), measurements of partial pressure of ammonia (Konowalov, *Z. physikal. Chem.*, 1898, **28**, 558; Gans, *Z. anorg. Chem.*, 1900, **25**, 236), thermochemical measurements (Berthelot and Delépine, *Compt. rend.*, 1899, **129**, 326; Bruni and Levi, *Gazzetta*, 1917, **47**, i, 259), and transference number determinations (Whitney and Melcher, *J. Amer. Chem. Soc.*, 1903, **25**, 70). The current view that silver exists in ammoniacal solutions as a complex kation, each silver atom being associated with two molecules of ammonia, originated in the work of Bodländer and Fittig (*Z. physikal. Chem.*, 1901, **39**, 597), who showed by an application of the mass law that the solubility of silver chloride in ammonia could be accounted for if the silver were assumed to pass into a complex ion, $Ag(NH_3)_x$, the values of x actually varying from 1·67 to 2·22. Little appears to be known of the process of formation of the complex, and consequently the experiments described in the second portion of this paper have been performed.

Experimental.

1. *Electrometric Titration with the Silver Electrode of Silver Nitrate with Sodium Hydroxide.*

The precipitation of silver oxide was studied by means of the following concentration cell, the $Ag|N/10\text{-}AgNO_3$ serving as the standard half-element; the other silver electrode dipped in the solution which was being titrated:

$$Ag\left|N/10\text{-}AgNO_3\right|\begin{array}{c}\text{saturated}\\ KNO_3\text{ solution}\end{array}\left|\begin{array}{c}100\text{ c.c. of }0{\cdot}02M\text{-}AgNO_3\\ +\ x\text{ c.c. of }0{\cdot}1N\text{-NaOH}\end{array}\right|Ag.$$

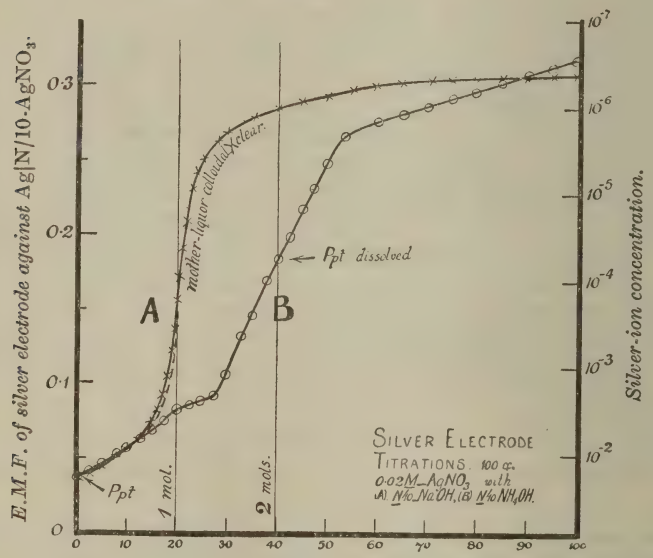
The alkali was added very slowly and before each measurement was made the mixture was thoroughly stirred. Steady and reproducible *E.M.F.*'s were readily obtained. The two electrodes, made from the same piece of silver wire, were fused into glass tubes so that lengths of 2 cm. were exposed, and covered electrolytically with layers of finely divided silver from silver nitrate solution. Checked against a normal calomel electrode, saturated potassium nitrate being used as junction liquid, they gave a normal electrode potential

of 0·802 volt at 20°, in good agreement with the accepted value, 0·80. *E.M.F.* of Ag|N/10-$AgNO_3$|Saturated KNO_3|N-Calomel = 0·456 volt. Therefore E_h of Ag|N/10-$AgNO_3$ = 0·739. The dissociation of silver nitrate in N/10-solution being taken as 81·4%, $E_h = 0{\cdot}739 = {}_oE_h + RT \log [Ag^{\cdot}]/nF = {}_oE_h - 0{\cdot}063$; and consequently ${}_oE_h =$ 0·802 volt. The results obtained are plotted in Fig. 1, curve A.

The precipitate formed during the addition of the first 10 c.c. of alkali was white, but immediately became brown. A little remained in colloidal suspension until 7 c.c. more than the theoretical amount of alkali had been added.

The dotted line (Fig. 1) represents the change in silver-ion con-

FIG. 1.



centration calculated on the assumption that precipitation had effected a proportional diminution in the silver-ion concentration of the mother-liquor. The observed and the theoretical curves are coincident for the first 15 c.c. of alkali, but thereafter the dotted curve lies a little lower, which may be due to the carrying down of silver nitrate by the precipitate. Silver nitrate in the precipitate would tend to become a "solution link" (compare Thomas and Freiden, *J. Amer. Chem. Soc.*, 1923, **45**, 2522) and its presence would account for some silver oxide remaining in colloidal solution. Much of the undecomposed silver nitrate was readily attacked, as will be seen from the great change in silver-ion concentration which took place at the point corresponding to the stoicheiometrical

amount of sodium hydroxide. There probably still remained a trace of unattacked silver nitrate, although too small to be shown in the diagram, for the colloidal solution was not decomposed until 7 c.c. excess of alkali had been added. This suggestion may account for the high initial values of the solubility product of silver hydroxide given in Table I. If the formation of such a colloidal solution is due to a stabilising influence, tending to increase the solubility of the dispersed particles, such as may be created by the silver oxide particles containing some undecomposed silver nitrate, it would be expected that silver hydroxide would be more soluble when a part of it is in colloidal solution than when it is not.

The silver-ion concentrations were calculated from the equation $E_{obs.} = -0{\cdot}063 - 0{\cdot}058 \log [Ag^{\cdot}]$, and the hydroxyl-ion concentrations from the excess of alkali added, complete dissociation being assumed. On introducing corrections for dissociation, the solubility products are diminished by about $0{\cdot}1 \times 10^{-8}$ in every case.

TABLE I.

v = cc. of 0·1*N*-sodium hydroxide added.

v.	*E.M.F.*	$[Ag^{\cdot}] \times 10^{7}$.	$[OH'] \times 10^{4}$.	$[Ag^{\cdot}][OH'] \times 10^{8}$.	v.	*E.M.F.*	$[Ag^{\cdot}] \times 10^{7}$.	$[OH'] \times 10^{4}$.	$[Ag^{\cdot}][OH'] \times 10^{8}$.
20·5	0·171	925	4·15	3·84	35·0	0·279	12·7	111	1·41
21·0	0·191	418	8·26	3·45	40·1	0·285	9·98	143	1·43
22·0	0·208	212	16·4	3·48	50·1	0·293	7·46	200	1·49
23·0	0·231	85·3	24·4	2·08	60·0	0·300	5·51	250	1·38
24·0	0·241	57·3	32·3	1·85	71·1	0·303	4·89	289	1·46
25·0	0·250	40·2	40·0	1·68	80·0	0·303	4·89	333	1·63
27·62	0·263	24·0	59·4	1·43	90·0	0·3045	4·60	368	1·70
30·0	0·269	18·9	76·9	1·45	100·0	0·306	4·35	400	1·74

The average value of $[Ag^{\cdot}][OH']$ is $1{\cdot}51 \times 10^{-8}$ for the last ten determinations and $1{\cdot}44 \times 10^{-8}$ for values of v from 27·62 to 71·1. Böttger (*Z. physikal. Chem.*, 1903, **46**, 521) found the value $1{\cdot}52 \times 10^{-8}$ from conductivity measurements at 20°, and Jellinek and Gordon (*ibid.*, 1924, **112**, 212) the lower values 5·5 and $7{\cdot}3 \times 10^{-9}$ from *E.M.F.* measurements of $Ag|Ag_2O,xNaOH$. The cause of the discrepancy between these two results, and of their exceptional lowness, can be traced to the erratic behaviour of the silver electrode in presence of silver oxide in alkaline solutions, which Luther and Pokorný (*Z. anorg. Chem.*, 1908, **57**, 290) and Buehrer (cited in Lewis and Randall's "Thermodynamics," 1923, p. 483), who observed it, are inclined to attribute to reduction of the silver oxide at the expense of the electrode.

The behaviour of the $Ag|Ag_2O$,NaOH electrode during the titration may perhaps best be studied from a consideration of the voltages of the oxygen–hydrogen cell, as several attempts have been made to arrive practically at its *E.M.F.* through measurements

of the silver electrode in question. Nernst and Wartenberg (*Z. physikal. Chem.*, 1906, **56**, 534) found, by extrapolation from the results obtained in their classical researches on the dissociation of steam at high temperatures, that the potential difference of the oxygen–hydrogen cell at the ordinary temperature could be calculated from the expression $E.M.F. = 1{\cdot}232 - 0{\cdot}00085\ (t° - 17)$, and therefore the *E.M.F.* at 20° should be 1·229 volts. G. N. Lewis (*J. Amer. Chem. Soc.*, 1906, **28**, 158) calculated that the *P.D.* of $O_2|NaOH,Ag_2O|Ag$ is 0·049 volt at 25° from the dissociation pressures of silver oxide at high temperatures, which have since been confirmed by Keyes and Hara (*ibid.*, 1922, **44**, 479), the essential assumption being that no allotropic change in the silver oxide takes place on heating. Hence, the *E.M.F.* of $O_2| - |H_2$ being 1·229 volts at 20°, and calculation showing that the *E.M.F.* of $O_2|NaOH,Ag_2O|Ag$ at 20° is the same as at 25°, the *E.M.F.* of $Ag|Ag_2O,NaOH|H_2$ should be 1·180 volts at 20°. Using Böttger's value of the solubility product of silver hydroxide at 25°, Lewis calculated that the *P.D.* at 25° of the last combination should be 1·168 volts, and consequently that of the oxy-hydrogen cell should be 1·217 volts. Converted by means of the temperature coefficient given in Nernst and Wartenberg's equation, these *P.D.*'s become 1·172 and 1·221 volts at 20°, respectively. Luther and Pokorný (*loc. cit.*) found by direct experiment that the initial voltage of $Ag|Ag_2O$(electrolytically prepared),$NaOH|H_2$ was 1·172 volts at 25° (*i.e.*, 1·176 volts at 20°).

Table II gives the *P.D.*'s of the $Ag|Ag_2O,NaOH|H_2$ combination calculated for various stages of the titration, from which the *E.M.F.*'s of the oxygen-hydrogen cell were obtained by adding 0·049 volt (*vide supra*).

TABLE II.

C.c. of N/10-NaOH.	E_h $Ag|Ag_2O,NaOH.$	E_h $H_2|NaOH.$	*E.M.F.* $Ag|Ag_2O,NaOH|H_2.$	*E.M.F.* $O_2| - |H_2.$
20·5	0·568	−0·621	1·189	1·238
22·0	0·531	−0·655	1·186	1·235
25·0	0·489	−0·681	1·167	1·216
30	0·470	−0·700	1·170	1·219
40	0·450	−0·710	1·164	1·213
60	0·439	−0·724	1·163	1·212
80	0·436	−0·731	1·167	1·216
90	0·435	−0·735	1·170	1·219
100	0·433	−0·736	1·169	1·218
			Mean 1·167	1·216

The E_h of $Ag|Ag_2O,NaOH$ was found by subtracting the observed voltages given in Table I from 0·739, the E_h of $Ag|N/10\text{-}AgNO_3$, it being assumed that the junction of saturated potassium nitrate solution reduced the diffusion potential to negligible dimensions.

The E_h's of the hydrogen electrode in alkaline solutions were calculated from the formula $E_h = 0{\cdot}0581 \log [H^\cdot]$, K_w at 20° being $10^{-14{\cdot}07}$, and the sodium hydroxide being regarded as completely dissociated. On correcting for ionisation, the values become 2 to 3 millivolts less negative.

The first two *P.D.*'s of the oxygen–hydrogen cell are greater than the value, 1·229 volts, found by Nernst and Wartenberg (*loc. cit.*). The discrepancy may be due to a slightly increased solubility of the silver oxide through some having been in colloidal solution, and possibly also to some extent to the fact that precipitation had only just ended and consequently any reduction which might have taken place would be at a minimum.

Save for the first two values, the *E.M.F.*'s of the $Ag|Ag_2O,NaOH|H_2$ range from 1·163 to 1·170 volts. The average value, 1·167 volts, is 13 millivolts less than the one given by Nernst and Wartenberg, 5 mv. less than that of Lewis, and 9 mv. less than the initial value of Luther and Pokorný for electrolytic silver oxide.

Rørdam (*Z. physikal. Chem.*, 1921, **99**, 474) has determined the *P.D.*'s of many cells, $Ag|Ag_2O,alkali|H_2$, in which both barium and sodium hydroxides were employed and also samples of silver oxide which had been subjected to a variety of treatments. With precipitated oxides, the *E.M.F.*'s varied from 1·137 to 1·155 volts at 25°, or from 1·141 to 1·159 at 20°, the higher values being obtained with those oxides which had not been separated from the solutions from which they were precipitated. On the other hand, by electrolysing a sodium hydroxide solution between a platinised platinum kathode and a silver anode, he found that, after the current had been flowing for a few minutes, the *E.M.F.* measured immediately after it was stopped varied between 1·171 and 1·177 volts at 25° (*i.e.*, 1·175 to 1·181 volts at 20°), the kathode becoming in effect a hydrogen electrode. The highest value agreed with the value extrapolated from the work of Nernst and Wartenberg and Lewis.

The values given in Table II of the *E.M.F.*'s of the $Ag|Ag_2O,NaOH|H_2$ fall between those indicated by Rørdam's measurements. It is significant that the highest value for precipitated oxides, corresponding to 1·159 volts at 20°, indicated by Rørdam's work was obtained with silver oxide which had not been removed from the solution in which it was precipitated. The higher *E.M.F.*'s of the present author may be due to the fact that they were measured within a few moments of precipitation. If the lowness of the $Ag|Ag_2O,NaOH$ results is due, as suggested by Buehrer and Luther and Pokorný, to reduction, it would appear that the higher values obtained in this work were due to reduction having taken place to a smaller extent than in the experiments of Rørdam.

Strangely enough, Rørdam attributed the low results given by precipitated oxides, as compared with those given by the electrolytic oxide, to the existence of two different modifications of silver oxide, having different dissociation pressures, and by means of the Nernst heat theorem he calculated the transformation temperature to be 132°. For the purpose of calculation, he took 1·143 volts at 25° to be the *E.M.F.* of

$$Ag|Ag_2O(\text{precipitated}),NaOH|H_2$$

in spite of the wide variation in his experimental values, *viz.*, from 1·137 to 1·155. He considered that the precipitated oxides were the forms stable below 132° and that the electrolytic oxide was metastable at the ordinary temperature but stable above 132°. For this reason, the method adopted by Lewis in his calculation of the *P.D.* of $O_2|NaOH,Ag_2O|Ag$ was held to be inadmissible. This hypothesis does not account for the *E.M.F.*'s found in this work, which, as already stated, lie between those obtained with the two supposed forms of silver oxide. The variable results obtained with the $Ag|Ag_2O$,alkali electrode, especially after standing for some time, appear to be best accounted for by reduction. The low solubility products obtained by Jellinek and Gordon (*loc. cit.*) were probably due to this cause, especially if the exceptionally low values of the extrapolated *P.D.*'s of the $Ag|Ag_2O,NaOH|H_2$ cell be considered, in one case 1·150 volts at 20° and in another 1·139.

TABLE III.

Temp.	Method.	Mols. AgOH per litre $\times 10^4$.	$[Ag^{\cdot}][OH']$ $\times 10^8$.	Observer.
20°	Analysis.	1·48—1·85	2·2—3·4	Whitby, 1910.
	Conductivity.	1·23	1·52	Böttger, 1903.
	E.M.F.	0·7—0·9	0·6—0·7	Jellinek and Gordon, 1924.
	,,	1·2	1·5	Britton, this paper.
	Calculation.	1·67	2·78	,, ,,
25°	Analysis.	1·73—2·26	3·0—5·1	*Noyes and Kohr, 1902.
	,,	4·3—5·9	18·6—34·9	†Rebière, 1915.
	Equilibria.	1·5	2·25	Noyes and Kohr, 1902.
	,,	1·8	3·2	Abegg and Cox, 1903.
	Conductivity.	1·39	1·93	Böttger, 1903.
	E.M.F.	0·95	0·9	‡Calc. from the data of Abegg and Cox, 1903.
	Calculation.	1·66	2·74	Britton, this paper.

* *J. Amer. Chem. Soc.*, 1902, **42**, 336.

† Rebière's values (*Bull. Soc. chim.*, 1915, **17**, 309) are probably twice too high, for he states that his lowest value agrees with Noyes's average value.

‡ Rørdam showed that the *E.M.F.* of $Ag\,Ag_2O,N/10\text{-}Ba(OH)_2|H_2$ (compare Abegg and Cox, *Z. physikal. Chem.*, 1903, **46**, 1) on which this calculation was based was 1·140 volts, thereby accounting for the low value of the solubility product.

The solubility products given in Table I, when considered in connexion with the *E.M.F.*'s of the $Ag|Ag_2O,NaOH|H_2$ combination, appear to be lower than would be expected from the fundamental calculations of Nernst and Wartenberg and Lewis. Had the electrode been satisfactory, the potential difference of the combination should have been $1{\cdot}229 - 0{\cdot}049 = 1{\cdot}180$ volts at 20°, from which it follows that $[Ag^{\cdot}][OH'] = 2{\cdot}78 \times 10^{-8}$ at 20°. The theoretical potential difference of $Ag|Ag_2O,H_2O|H_2$ at 25° is 1·176 volts, which gives $[Ag^{\cdot}][OH'] = 2{\cdot}74 \times 10^{-8}$ at that temperature.

Analytical determinations of the solubility of silver oxide have given widely differing results, which were dependent on the length of time allowed for the attainment of equilibrium and on the method of preparation of the oxide. Whitby (*Z. anorg. Chem.*, 1910, **47**, 107) found that at 20° silver oxide required 14 days to attain equilibrium with water. Table III gives a comparison of the results obtained at 20° and 25° by chemical and physical methods. The solubility products have been calculated on the assumption that the dissolved silver oxide was completely ionised.

At both temperatures the data obtained by direct analysis are higher than those obtained by physical methods. This may perhaps be partly due to incomplete dissociation of the silver oxide. The variable results obtained by *E.M.F.* methods show that these are unsatisfactory. The author's value at 20° is probably low and yet agrees with that of Böttger. Böttger's value at 25° was used by Lewis in his fundamental calculation of the *E.M.F.* of the oxygen–hydrogen cell, and, contrary to the contention of Rørdam, the low value he obtained is probably thus accounted for.

2. *Electrometric Titrations of Silver Nitrate with Ammonium Hydroxide by means of* (a) *the Oxygen Electrode, and* (b) *the Silver Electrode.*

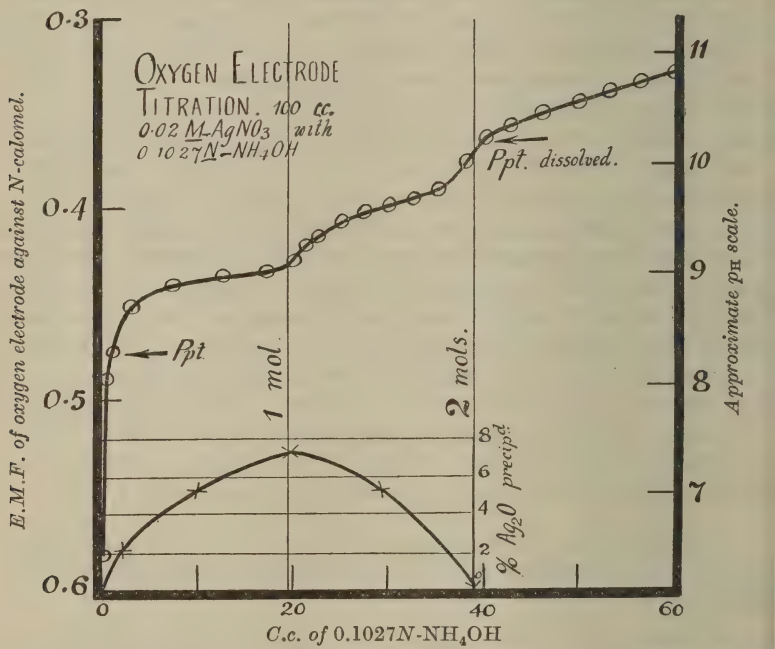
Although the oxygen electrode is affected by the presence of silver oxide, it can be used to indicate any pronounced changes in hydrogen-ion concentration which may take place when alkalis are added to silver salt solutions (this vol., p. 2148). The change in hydrogen-ion concentration occurring during the formation of the silver ammonia complex from silver nitrate and ammonia has therefore been followed with its aid.

0·02*M*-Silver nitrate (100 c.c.) was titrated with 0·1027*N*-ammonium hydroxide at 18°, the oxygen electrode and the normal calomel electrode being used with saturated potassium nitrate solution as junction liquid. In Fig. 2, the observed *E.M.F.*'s are plotted against the quantities of ammonia added. The proportional hydrion scale affixed to the diagram is based on colorimetric

measurements, by Gillespie's drop-method (*J. Amer. Chem. Soc.*, 1920, **42**, 742), of the hydrion concentrations of the solution at the beginning and the end of the titration. The scale showed hydrion concentrations at various stages of the titration which were in accord with those given by indicators.

The curve shows that the first drop of ammonia produced a sudden increase in p_H and that precipitation began when 1 c.c. had been added. The addition of more ammonia caused a further diminution in hydrogen-ion concentration until the p_H (approx. 9)

FIG. 2.



was reached at which silver oxide is normally precipitated. The change thereafter was a gradual one, until 1 mol. of ammonia (per mol. of silver nitrate) had been added; a small but definite inflexion then occurred, and was followed by another when 2 mols. of ammonia had been added. At this stage the precipitate had completely dissolved. Draper (*loc. cit.*) noted that solutions containing the reactants in these proportions were strongly alkaline to turmeric and phenolphthalein, *i.e.*, above p_H 8.

It might be imagined from the nature of the curve that the first section, corresponding to the addition of the first mol. of ammonia, represents the complete precipitation of silver oxide, and the second section its reaction with one mol. of ammonia to form a soluble

monoammino-silver complex. The precipitation, however, was far from complete during the first part; and if a little, but sufficient, nitric acid had been added to a silver nitrate solution treatment with ammonia produced no precipitate. Moreover, moist silver oxide is readily soluble in ammonium nitrate solution, and in an amount that suggests the formation of $AgNO_3,NH_3$. The silver oxide precipitated on mixing equal volumes of N/10-silver nitrate and N/10-sodium hydroxide dissolved completely at room temperature in quantities of N/20-ammonium nitrate corresponding to the ratios 1 mol. AgOH : 1·1—1·2 mols. NH_4NO_3. The solutions had p_H about 8 and did not decompose on boiling. The silver-ion concentration of the solutions was comparatively large, *e.g.*, a solution composed of 20 c.c. of 0·1N-sodium hydroxide, 20 c.c. of 0·1N-silver nitrate, and 45 c.c. of 0·05N-ammonium nitrate contained 33·5% of the total silver present as silver ions. This may have been due to the presence of a highly dissociated monoammino-silver complex or of some silver nitrate and some diammino-complex.

Reychler (*Ber.*, 1883, **16**, 990) and Draper (*loc. cit.*) found that ammonia, if added in small quantities, caused partial precipitation of silver oxide from silver nitrate solution. In order to study this reaction more fully, the percentage amounts of silver oxide precipitated at different stages of the titration were determined. The results are in Table IV, and are shown diagrammatically in Fig. 2.

TABLE IV.

C.c. of 0·1027N-NH_4OH.	Mols. NH_4OH/ Mols. $AgNO_3$.	Ag_2O pptd. %.	Ppted. Ag_2O as percentage of the amount theor. precipitable.
1·95	0·1	2·2	22·0
9·8	0·5	5·3	10·6
19·5	1·0	7·3	7·3
29·3	1·5	5·3	
39·0	2·0	0	

No precipitation with ammonia occurred when the solution contained nitric acid in quantities greater than 0·05 mol. for 1 mol. of silver nitrate.

It appears that, although the solution had attained the p_H necessary for the precipitation of silver oxide, another reaction was taking place which withdrew from the solution some of the silver ions that ordinarily would have been precipitated. This may be seen from curve B in Fig. 1, which represents the titration of 100 c.c. of 0·02M-silver nitrate with N/10-ammonia with the aid of the silver electrode, carried out at 18° in the same way as the sodium hydroxide titration. The portions of the curves A and B corresponding to the addition of the first 15 c.c. of alkali are almost identical in spite of the partial precipitation produced by the ammonia. This

indicates that silver ions were being removed from solution mainly owing to complex formation. A small inflexion occurred when 1 mol. of ammonia had been added. Calculation from the data of Figs. 1 and 2 shows that the product $[Ag^{\cdot}][OH']$ became less and less during the addition of the second molecule of ammonia; when the addition was complete, its value was $0{\cdot}6 \times 10^{-8}$, which is less than the solubility product of silver hydroxide and thus accounts for the re-solution. The main inflexion occurred when 2 mols. of ammonia had been added. Bruni and Levi (*Gazzetta*, 1917, **47**, i, 259) made, among their measurements with the silver electrode, four on solutions containing less than 2 mols. of ammonia for 1 mol. of silver nitrate. Their results show that a sharp diminution in silver-ion concentration takes place when between 1·5 and 2 mols. of ammonia have been added.

The inflexion (Fig. 2) which occurred when 1 mol. of ammonia had been added may probably be accounted for by the fact that at that point the precipitation reaction stopped, and consequently the destruction of hydroxyl ions ceased. The slight inflexion in the silver-ion curve (B, Fig. 1) may be due to the two reactions, taking place during the addition of the first molecule of ammonia and causing precipitation and complex formation, being followed by complex formation only, which effects solution of the precipitate.

An attempt has been made to account for the silver-ion concentrations measured during the addition of the first 2 mols. of ammonia. The reactions were assumed to be (1) $AgNO_3 + NH_4OH \longrightarrow AgOH + NH_4NO_3$, and (2) $AgNO_3 + 2NH_3 \rightleftharpoons Ag(NH_3)_2NO_3$. The amount of ammonia required for the precipitation of the silver oxide having been subtracted from the total amount of ammonia added, the remainder was regarded as having been converted entirely into the complex salt $Ag(NH_3)_2NO_3$. The concentration of silver nitrate originally present being known, the concentration of unchanged silver nitrate could be calculated. The results are in Table V. The concentrations of free ammonia given in the last column were calculated from the expression $[Ag^{\cdot}][NH_3]^2/[Ag(NH_3)_2^{\cdot}] = 2{\cdot}2 \times 10^{-8}$ (*vide infra*).

TABLE V.

NH_4OH added.						
C.c.	Mols. per mol. of $AgNO_3$.	Conc. of Ag ions found $\times 10^4$.	Ag_2O ppted. %.	Conc. of $Ag(NH_3)_2NO_3$ $\times 10^4$.	Conc. of $AgNO_3$ $\times 10^4$.	Calc. conc. of free NH_3 $\times 10^4$.
2	0·1	170	2·2	7·6	180	0·21
10	0·5	85	5·3	41	130	1·0
20	1·0	30	7·3	77	77	2·4
30	1·5	12	5·3	110	34	4·5
40	2·0	0·57	0	140	0	23

It will be observed that the concentrations of silver ions and silver nitrate were of the same order, although the former became appreciably smaller as the quantity of added ammonia increased. The dissociation constant of ammonium hydroxide being taken as $2{\cdot}3 \times 10^{-5}$, the hydroxyl-ion concentration in equilibrium with the free ammonia present when 2 mols. had been added was $10^{-3{\cdot}64}$, and therefore p_H was 10·5, as compared with 10·2 shown by the scale in Fig. 2. If it be assumed that the concentration of ammonium nitrate in the solution when 1·5 mols. of ammonia had been added was equivalent to the amount of silver oxide precipitated, it can be shown that the amount of free ammonia, $4{\cdot}5 \times 10^{-4}$, should have produced p_H 9·3 (9·6; Fig. 2). The hydrogen-ion concentration prevailing in the earlier part of the titration was undoubtedly controlled by the hydroxyl ions originating from the precipitated silver oxide. The effect of a little nitric acid in a silver nitrate solution in preventing the precipitation of silver oxide with ammonia appears to be due to the depressing influence of the ammonium nitrate on the ionisation of the ammonium hydroxide.

It thus seems probable that the complex silver compound ultimately formed required 2 mols. of ammonia for its formation. The results in Table VI refer to the solutions which contained ammonia in excess of 2 mols. For the purpose of calculation, the ammonia in excess of 2 mols. was assumed to be in the uncombined state, the small dissociation of the ammonium hydroxide was disregarded, and the complex silver salt was taken as being completely dissociated thus: $Ag(NH_3)_2NO_3 \rightleftharpoons Ag(NH_3)_2^{\cdot} + NO_3'$. The data used are those represented graphically in curve B (Fig. 1), and the concentration of silver ions was calculated from the formula $E = -0{\cdot}063 - 0{\cdot}0577 \log [Ag^{\cdot}]$.

TABLE VI.

$NH_3/AgNO_3$.	C.c. of $N/10$-NH_4OH.	*E.M.F.*	$[Ag^{\cdot}]$.	$[Ag(NH_3)_2^{\cdot}] \times 10^5$.	$[NH_3]$.	$K = [Ag^{\cdot}][NH_3]^2/[Ag(NH_3)_2^{\cdot}] \times 10^8$.
2·26	45·1	0·217	$1{\cdot}40 \times 10^{-5}$	13·9	0·0035	1·26
2·5	50·0	0·248	$4{\cdot}07 \times 10^{-6}$	13·3	0·0067	1·36
3·0	60·0	0·275	$1{\cdot}39 \times 10^{-6}$	12·5	0·0125	1·74
3·5	70·0	0·286	$9{\cdot}0 \times 10^{-7}$	11·8	0·0177	2·38
4·0	80·0	0·295	$6{\cdot}3 \times 10^{-7}$	11·1	0·0222	2·78
4·5	90·0	0·307	$3{\cdot}8 \times 10^{-7}$	10·5	0·0263	2·50
5·0	100·0	0·317	$2{\cdot}6 \times 10^{-7}$	10·0	0·030	2·33
104	—	0·490	$2{\cdot}9 \times 10^{-10}$	9·5	0·971	2·90
					Mean	2·2

The values of K appear to confirm the existence of the diammino-silver compound in ammoniacal solutions. The first three low values of K refer to solutions in which a rapid change in silver-ion concentration was taking place, as shown in curve B (Fig. 1).

These values being omitted, the table shows that there is little variation in the constant, even although the molar ratio $NH_3/AgNO_3$ varies from 2 to 104. Calculation from Bruni and Levi's *E.M.F.* measurements (*loc. cit.*) shows not only that the silver-ion concentration in ammoniacal solutions becomes extremely small, but also that the constant K of the supposed complex kation is similar to that found above. They measured the *E.M.F.*'s of a series of cells of the type $Ag\left|\begin{matrix}N/10\text{-}AgNO_3\\ xN\text{-}NH_4OH\end{matrix}\right|N/10\text{-}NaNO_3\left|N/10\text{-Calomel}\right.$ (A) at 15°. The *E.M.F.* of the combination $Ag|N/10\text{-}AgNO_3|N/10\text{-}NaNO_3|N/10$-Calomel was 0·407 volt (B). The difference of the *E.M.F.*'s of A and B gives the *E.M.F.* of the concentration cell $Ag\left|\begin{matrix}N/10\text{-}AgNO_3\\ xN\text{-}NH_4OH\end{matrix}\right|N/10\text{-}NaNO_3\left|N/10\text{-}AgNO_3\right|Ag$, from which the concentrations of silver ions were found by means of $E = -0{\cdot}063 - 0{\cdot}0571 \log [Ag^{\cdot}]$. Table VII was compiled from the measurements of Bruni and Levi.

TABLE VII.

$NH_3/AgNO_3$.	$[Ag(NH_3)_2^{\cdot}]$.	Free NH_3.	*E.M.F.* against $N/10$-Cal.	$[Ag^{\cdot}]$.	$K=[Ag^{\cdot}][NH_3]^2/[Ag(NH_3)_2^{\cdot}]$ $\times 10^8$.
2·5	0·1	0·05	+0·111	$5{\cdot}8 \times 10^{-7}$	1·45
4·0	0·1	0·2	+0·049	$4{\cdot}9 \times 10^{-8}$	1·95
5·0	0·1	0·3	+0·029	$2{\cdot}2 \times 10^{-8}$	1·95
6·67	0·1	0·467	+0·002	$7{\cdot}6 \times 10^{-9}$	1·66
10	0·1	0·8	−0·017	$3{\cdot}4 \times 10^{-9}$	2·19
20	0·1	1·8	−0·055	$7{\cdot}6 \times 10^{-10}$	2·46
30	0·1	2·8	−0·077	$3{\cdot}0 \times 10^{-10}$	2·35
40	0·1	3·8	−0·093	$1{\cdot}6 \times 10^{-10}$	2·35
50	0·1	4·8	−0·107	$9{\cdot}6 \times 10^{-11}$	2·19
60	0·1	5·8	−0·119	$7{\cdot}6 \times 10^{-11}$	2·57
70	0·1	6·8	−0·129	$6{\cdot}2 \times 10^{-11}$	2·82
80	0·1	7·8	−0·138	$5{\cdot}0 \times 10^{-11}$	3·02
100	0·1	9·8	−0·156	$3{\cdot}5 \times 10^{-11}$	3·31
				Mean	2·3

Bruni and Levi's data refer to solutions, decimolar with respect to silver nitrate, but the ammonia content of which varied continuously from 0·25 to 10·0N. The results in Tables VII and VIII show that silver nitrate solutions varying in concentration from 0·0095M to 0·1M, when rendered ammoniacal from 2- to 100-fold, contain the $Ag(NH_3)_2^{\cdot}$ kation, the dissociation constant of which is $2{\cdot}2 \times 10^{-8}$ approximately. It is probable that the base $Ag(NH_3)_2OH$ is much stronger than ammonium hydroxide and consequently the salt $Ag(NH_3)_2NO_3$ exists in solution.

Bruni and Levi also measured the potential differences between a silver electrode immersed in various ammoniacal solutions of silver nitrite and a decinormal calomel electrode at 15°, using $N/10$-sodium nitrite as junction liquid. In view of the stability of

the diammino-silver kation when attached to the nitrate ion, the data on nitrite solutions were considered of especial interest in that they might serve to show the behaviour of the complex kation when combined with another anion. Its dissociation constant has been calculated and the results obtained are in Table VIII. The silver-ion concentrations were calculated from E (obs.) = 0·463 − 0·0571 log [Ag$^{\cdot}$], in which the ${}_{o}E_{h}$ of silver was taken as 0·800 volt, and E_h of N/10-calomel as 0·337 volt.

TABLE VIII.

$NH_3/AgNO_2$.	$[Ag(NH_3)_2^{\cdot}]$.	Free NH_3.	*E.M.F.* against N/10-Cal.	[Ag$^{\cdot}$].	$K=[Ag^{\cdot}][NH_3]^2/[Ag(NH_3)_2^{\cdot}]$ $\times 10^8$.
2·5	0·02	0·01	+0·169	$6·9 \times 10^{-6}$	3·46
4·1	0·02	0·0407	+0·098	$4·1 \times 10^{-7}$	3·37
5	0·02	0·060	+0·076	$1·7 \times 10^{-7}$	2·99
6·7	0·02	0·0933	+0·041	$4·1 \times 10^{-8}$	1·77
10	0·02	0·160	+0·019	$1·7 \times 10^{-8}$	2·17
20	0·02	0·360	−0·019	$3·6 \times 10^{-9}$	2·36
30	0·02	0·559	−0·043	$9·8 \times 10^{-10}$	1·52
40	0·02	0·760	−0·055	$8·7 \times 10^{-10}$	2·52
50	0·02	0·960	−0·065	$5·6 \times 10^{-10}$	2·59
				Mean	2·5

The results in Table VIII show that the silver-ion concentrations in ammoniacal solutions of silver nitrite are due to the dissociation of a diammino-silver complex, the dissociation constant of which is $2·5 \times 10^{-8}$, and is therefore independent of the anion.

Kohlschütter and Fischmann (*Annalen*, 1912, **387**, 94) made some electrometric determinations on ammoniacal solutions of silver nitrate, but their data, on calculation, fail to give any constancy for K. The only other solutions in which the existence of the complex kation has been established by proving that K is a constant are ammoniacal solutions of silver chloride, which Bodländer and Fittig (*Z. physikal. Chem.*, 1902, **39**, 597) found to give K equal to $7·88 \times 10^{-8}$, and ammoniacal solutions of silver oxide, for which Euler (*Ber.*, 1903, **36**, 1854, 2878) obtained values of K ranging from $3·4$ to $6·4 \times 10^{-8}$ at 16° when the ammonia was in large excess, and from $1·5$ to $1·67 \times 10^{-8}$ when the excess was small.

Summary.

(1) The precipitation of silver oxide with sodium hydroxide has been studied electrometrically, and the solubility product [Ag$^{\cdot}$][OH$'$] calculated.

(2) The behaviour of the silver electrode in alkaline solutions containing suspended silver oxide has been discussed, and Rørdam's view that two modifications of silver oxide exist shown to be improbable.

(3) The value of the *E.M.F.* of the oxygen–hydrogen cell

found by Lewis is low, probably because a low value was taken for $[Ag^{\cdot}][OH']$.

(4) The reaction between silver nitrate and ammonia has been studied and further evidence of the existence of the complex kation $Ag(NH_3)_2^{\cdot}$ obtained.

The author takes this opportunity to thank Professor J. C. Philip, F.R.S., for facilities in carrying out this work, and the Department of Scientific and Industrial Research for a personal grant.

Imperial College of Science and Technology,
London. [*Received, August 14th*, 1925.]

NOTES.

Preparation of p-*Bromophenylhydroxylamine by the Emulsification Process. A Modification.* By Robert Downs Haworth and Arthur Lapworth.

It has been found that the reduction of pure *p*-bromonitrobenzene is often quite unsuccessful if carried out as previously described (J., 1921, **119**, 770). The following modification of the original method, however, usually gives a yield of *p*-bromophenylhydroxylamine nearly the same as that originally obtained but involves the use of more solvent benzene and preferably also more reducing solution. It is essential that the sodium sulphide crystals used in making the reducing solution should be of good quality.

p-Bromonitrobenzene (5 g.), benzene (40 c.c.), the hydrosulphide solution (120 g., prepared as formerly described, *loc. cit.*, p. 769), and calcium chloride (5 g., in a little water) are emulsified. Crystals soon separate and, after 1½ hours, solid ammonium chloride (5 g.) is added, the whole shaken, and the precipitated *p*-bromophenylhydroxylamine (about 2·9 g.) collected and washed with water. The benzene layer of the filtrate is separated, washed with water, dried over anhydrous sodium sulphate, and carefully diluted with petroleum (b. p. 40—60°); a further crop (about 0·5 g.) of the hydroxylamine is then obtained.

Three experiments carried out in the above way gave total yields of 2·7 g., 3·4 g., and 3·3 g., respectively, of *p*-bromophenylhydroxylamine. With the smaller quantity (52 g.) of sodium hydrosulphide solution previously advised, the yields in five experiments were 2·4—3·2 g.—The University, Manchester. [*Received, November 24th*, 1925.]

Action of Hydrazine Hydrate on Phenanthraquinone. A Correction. By SIKHIBHUSHAN DUTT.

IT was stated by Dutt and Sen (J., 1923, **123**, 3420) that phenanthrone is the sole product obtained from phenanthraquinone by the action of hydrazine hydrate. In subsequent experiments with commercial hydrazine hydrate (50%) 9 : 10-dihydroxyphenanthrene (m. p. 147°) was almost exclusively obtained instead of phenanthrone.

Fortunately, a small quantity of the original "hydrazine hydrate" in a sealed tube was available and this was found to be incorrectly labelled, the substance being actually pure anhydrous hydrazine. Further experiments have shown that, when anhydrous hydrazine is allowed to react with phenanthraquinone in absolute alcohol, phenanthrone is obtained in good yield and that, when small quantities of moisture are present or when ordinary commercial hydrazine hydrate is employed, 9 : 10-dihydroxyphenanthrene is almost the sole product.

The error was made through unavoidable circumstances, but is none the less regretted.—IMPERIAL COLLEGE, SOUTH KENSINGTON, S.W. 7. [*Received, November 28th*, 1925.]

The Aluminioxalates of some Optically Active Bases. By THOMAS BRUCE CHILD, ELWYN ROBERTS, and EUSTACE EBENEZER TURNER.

COMPOUNDS of the aluminioxalate type, derived from the acid $H_3Al(C_2O_4)_3$, should be capable of resolution into optically active forms. This has been attempted by means of active bases.

Strychnine Aluminioxalate.—Barium aluminioxalate (Burrows and Walker, J., 1923, **123**, 2738) twice crystallised from water was warmed with the calculated quantity of aqueous strychnine sulphate. The precipitate of barium sulphate and strychnine aluminioxalate was extracted with boiling water, and the extract allowed to crystallise. Different crops had $[\alpha]_D^{20°}$ $-24{\cdot}0°$ to $-21{\cdot}0°$ in 50% aqueous acetone, and formed slender, colourless needles, very sparingly soluble in water [Found : strychnine, 63·0; C_2O_4, 16·6. $C_{21}H_{22}O_2N_2)_3,H_3Al(C_2O_4)_3,16H_2O$ requires strychnine, 63·4; C_2O_4, 6·7%]. When these salts were recrystallised, partial decomposition occurred with formation of strychnine oxalate and aluminium hydroxide, and no conclusions can be drawn in connexion with any rotational differences observed.

When a solution of sodium aluminioxalate was treated with half its equivalent of aqueous strychnine hydrochloride a salt was obtained which had $[\alpha]_D^{20°}$ $-19{\cdot}0°$ in 50% aqueous acetone. It was treated with aqueous potassium iodide, and the precipitated strych-

nine hydriodide removed. The resulting solution of potassium aluminioxalate contained a trace of colloidal aluminium hydroxide, and what optical measurements were possible pointed to the inactivity of the solution.

Crystallisation of strychnine aluminioxalate from acetone gave crops of salt having slightly different specific rotations, but consistent results could not be obtained.

l-*Menthylamine Aluminioxalate.*—The barium salt was digested at 100° with an aqueous solution of the equivalent quantity (10 g.) of *l*-menthylamine, previously dissolved in the calculated quantity of dilute sulphuric acid. Sufficient water was added to keep all the menthylamine salt in solution, and after filtration from barium sulphate 17 g. of l-*menthylamine aluminioxalate* separated in well-defined prisms which were sparingly soluble in water [Found : *l*-menthylamine, 59·2; C_2O_4, 33·6. $(C_{10}H_{21}N)_3,H_3Al(C_2O_4)_3,H_2O$ requires *l*-menthylamine, 59·9; C_2O_4, 34·0%]. This salt had $[\alpha]_D^{20°}$ −28·5° in 50% aqueous acetone. Recrystallisation, which was accompanied by partial decomposition, gave no evidence of resolution.

Treatment of a concentrated solution of sodium aluminioxalate with one-third of the equivalent quantity of *l*-menthylamine sulphate gave a salt having a rotation practically identical with the above.

l-*Phenylethylamine Aluminioxalate.*—This salt was prepared by digesting the barium salt with the calculated quantity of aqueous *l*-phenylethylamine sulphate at 100° for about an hour, removing the barium sulphate, and evaporating to a small bulk under diminished pressure. It crystallised from water, in which it was very soluble, in colourless prisms. The main bulk of the salt had $[\alpha]_D^{20°}$ −3·00° in aqueous solution [Found : C_2O_4, 39·1.

$$(C_8H_{11}N)_3,H_3Al(C_2O_4)_3,H_2O$$

requires C_2O_4, 39·1%]. After it had been recrystallised four times from water, its rotation was not measurably affected (Found *l*-phenylethylamine, 53·0; C_2O_4, 39·2. Calc., *l*-phenylethylamine 53·7%).

Distrychnine potassium aluminioxalate and d-*phenylethylamine dipotassium aluminioxalate* were also prepared. Their specific rotations did not change as a result of repeated recrystallisation. *Cinchonidine aluminioxalate* was obtained as a gummy solid which could not be crystallised.

The authors wish to thank the Research Fund Committee of the Chemical Society for a grant by means of which the expense of this work has been met.—East London College, University of London. [*Received, September 19th,* 1925.]

OBITUARY NOTICES.

RICHARD BURTLES.

BORN MAY 25TH, 1900; DIED JULY 3RD, 1925.

RICHARD BURTLES was the younger son of the late Alderman Richard Burtles of Manchester. He was educated at Manchester Grammar School, and at the College of Technology, Manchester. He obtained the B.Sc. Tech. degree in July, 1921, being placed in the first (Honours) division, and was awarded a Manchester Education Committee Research Scholarship. This enabled him to devote a year to research, during which he carried out an investigation on the tautomerism of the diphenylglyoxalines, by which he earned the M.Sc.Tech. degree. He was then given a maintenance grant by the Department of Scientific and Industrial Research, and investigated the preparation of 2-aminoglyoxalines and their behaviour towards nitrous acid. The patience, skill, and enthusiasm which he showed in these researches led to his appointment, in July, 1924, as the writer's research assistant. In January, 1925, he took a position as chemist to the Goodrich Rubber Company, Ltd., of Leyland, and held this position until his death, which was due to a bicycle accident.

Burtles was elected a Fellow of the Chemical Society in May, 1923, and published three papers, jointly with the writer, in the *Journal* (1923, **123**, 361; 1925, **127**, 581, 2012). He was greatly interested in stained glass, no doubt owing to the fact that his father had been a glass manufacturer, and contributed articles on " The Colouring of Mediæval Glass " and " The Decay of Ancient Glass " to the *Journal of the Manchester University Science Federation* (1923, **2**, i, 18; 1924, **2**, ii, 62). He took a useful part in the social life of the college, becoming Secretary of the Manchester University Science Federation and also of the College of Technology Chemical Society, and was very popular with the staff and students.

During his school career, Burtles underwent training for military service in the Officers Training Corps, and reached the rank of lieutenant, but owing to his age he was not called upon to serve abroad.

Burtles married Vera, daughter of C. E. Chalmers, Esq., of Wellington, Salop, in July, 1924, and leaves a son, born a few days after his death.

F. L. PYMAN.

REGINALD ARTHUR JOYNER.

BORN JANUARY 10TH, 1887; DIED OCTOBER 7TH, 1925.

DR. R. A. JOYNER lost his life as the result of an accident on Wednesday, October 7th, 1925, through an explosion in the research laboratories of Messrs. Nobel's Explosives Co., Ltd.

Dr. Joyner studied at University College, Bristol, taking a London degree with Honours in Chemistry in 1909, followed by the M.Sc. degree of the newly-founded University of Bristol in 1910. His work during this period is recorded in three papers on amalgams of silver and tin published in the *Journal* of the Chemical Society. These exhibit his careful and thorough experimentation and stand unaltered. They form the accepted basis of the treatment of dental amalgams in modern courses on Dental Metallurgy.

Joyner proceeded as an 1851 Exhibition Scholar to Zürich and afterwards followed Bredig to the Technische Hochschule, Karlsruhe, where he qualified for the degree of Doctor of Engineering, which has seldom been obtained by students from abroad. Bredig recognised his exceptional ability and independent judgment. Joyner published two very neat experimental papers; one dealt with the affinity constant of hydrogen peroxide; the other, on the catalysis of camphorcarboxylic acid by bases in various solvents, further elucidated the remarkable parallelism between ordinary reactions and life processes, showing a mechanism through which optical activity may play its well-known rôle.

For 12 years Dr. Joyner served on the Research Staff of Messrs. Nobel's at Ardeer. Most of the important work which he carried out on such war-time problems as mustard gas and explosives is, of course, not available for publication, but an estimate of his unusual experimental skill and scientific acumen may be obtained from a study of the paper which he published in the *Journal* of the Chemical Society on the "Viscosity of Solutions of Cuprammonium." His skill in the field of chemical technology is well illustrated by his patented process for the continuous manufacture of hydrazine (Brit. Pat. No. 199750 of 1923).

Those who came in contact with Joyner must have realised that few scientists showed such whole-hearted devotion and enthusiasm. He had many other interests, having been versatile in athletics and a keen territorial officer for many years. His straightforward and unassuming personality gained him, not only esteem, but also affection from all who knew him. In spite of the tragedy of his loss at the age of thirty-eight his widow and three children can look back with pride on his devoted work in the cause of science.

J. W. McB.



Guglielmo Körner

[To face p. 2975.]

GUGLIELMO * KÖRNER.

BORN APRIL 20TH, 1839; DIED MARCH 29TH, 1925.

GUGLIELMO KÖRNER was born in Cassel on April 20th, 1839. Having completed his course at the Polytechnic, he decided to devote himself to chemistry and studied under Will, Kopp, and Engelbach at Giessen, where he graduated in 1860. He remained at Giessen as assistant for 3 years and shortly after spent a year as student under Kekulé at Ghent. Early in 1865 he became assistant to Professor Odling at St. Bartholomew's Hospital; but at the end of the year returned to Ghent as private assistant and secretary to Kekulé, remaining there until the end of 1867, when the latter was elected to the chair of chemistry at Bonn.

At this time Kekulé was engaged in developing his theory of the aromatic compounds and in preparing his treatise on the same subject, and with this work Körner was closely associated. It is well known that Kekulé regarded his theory merely as a philosophic system which connected in a simple fashion the many isolated facts of aromatic chemistry and served as a useful means of explaining their relations; but he failed to grasp to the full extent its practical consequences. Körner, with a clearer and broader outlook, foresaw the possibility of establishing the theory on a sound experimental basis.

During his stay at Ghent Körner found time to carry out a number of researches, the most important of which were "the synthesis of resorcinol" and one entitled "Faits pour servir à la détermination du lieu chimique dans la série aromatique," published in 1867. In the preface to the former he points out that Kekulé's theory involves two problems not yet solved. He says, "Dans l'étude des cas d'isomerie dans les substances aromatiques on peut conséquemment se poser deux problèmes principaux: on peut d'abord chercher à établir par expérience quels sont les corps de même constitution, c'est-à-dire, dans lesquels la substitution se fait à des places correspondantes; on peut ensuite spécifier davantage ces places *en cherchant par combien d'atomes d'hydrogène elles sont séparées entre elles.* Dans sa plus grande généralité, ce dernier problème pourrait s'appeler la détermination du *lieu chimique* de l'atome substituant. . . . La solution du second problème paraît à première vue inaccessible à l'expérience. Je pense toutefois qu'on pourrait y parvenir." He embodies here the idea which

* Körner was christened Wilhelm and, strictly speaking, should bear that Christian name; but as he lived most of his life in Italy and never returned to his native land and was known by and published under the name Guglielmo, it seems right so to designate him.

underlay his life's work. In the same paper he brought forward a new fact in support of Kekulé's theory: for he succeeded in adding to the few di-derivatives, then known in three isomeric forms, a new and third iodophenol.

In the second paper, published in 1867, he gives an indication of the principle upon which his method of orientation is based. "Suppose," he says, "that the three dihydroxybenzenes give the same trihydroxybenzene, by the introduction of a third hydroxyl, it is obvious that the three hydroxyls must occupy the positions 1, 2, 4. In short, it is only this arrangement of the three hydroxyls which can combine in one compound the three dihydroxy-derivatives." It must be remembered that at this time methods of orientation were largely speculative.* It is true that by a fortunate act of intuition Baeyer assigned the correct constitution to mesitylene and Graebe gave the true formula to phthalic acid; but, on the other hand, some of the suggestions were less happy. Quinol, for reasons into which we need not enter, was assumed to be an ortho-compound, salicylic acid a meta-compound, and ordinary dinitrobenzene a para-compound, and so forth, assumptions which subsequently led to ever increasing confusion as relationships became more clearly and closely established.

For reasons of health Körner left Ghent for Palermo in 1867 and entered the laboratory of Cannizzaro, where he continued to work indefatigably, collecting fresh experimental facts connected with the problem which he had set out to solve. In the two years which followed, this material had so far accumulated that Cannizzaro induced Körner to publish it, although the latter would have preferred to withhold it until it had reached a more complete form.

This memoir, which involved a stupendous amount of brilliant experimental work, appeared in 1869 in the *Giornale di Scienze Naturali ed Economiche* of Palermo under the title "Facts which serve for the determination of the chemical position in aromatic compounds." After a short introduction by Cannizzaro, the memoir begins with a clear account of Kekulé's theory on the constitution of benzene and the kinds of isomerism to which it gives rise. Körner shows that the non-existence of more than one monoderivative and the special kind of isomerism existing among the polysubstituents of benzene is based on the hypothesis of the equivalence of the six valencies of the carbon atoms of the

* An excellent account of the development of the views on orientation is given in Roscoe and Schorlemmer's "Treatise," vol. iii, part iii (Introduction) and also in the introduction by Richard Meyer to Erlenmeyer's "Lehrbuch der organischen Chemie," vol. ii (Leipzig, 1882).

nucleus and the relative positions occupied by two or more substituent elements or groups. He then proceeds to bring experimental evidence of the equivalence of the six atoms of hydrogen. Beginning with the three hydroxybenzoic acids, he shows that by eliminating carbon dioxide the same phenol results. Thus, the differences in the three acids must be due to the relative positions of the groups. By substituting chlorine for hydroxyl and replacing the halogen by hydrogen with the aid of sodium amalgam, he obtained the same benzoic acid in all three cases. These experimental facts, due partly to Körner and partly to Graebe and Beilstein, demonstrate completely the equivalence of three positions in the nucleus.

A fourth position was determined as follows: the nitroaniline (para) of Arppe can be transformed into chlorobromobenzene in two ways, either by substituting chlorine for the amino-group and bromine for the nitro-group or *vice versa*, and the same product results. As this nitroaniline can be proved to belong to the same series as one of the hydroxybenzoic acids, it follows that the position occupied by the phenol residue in the three acids is equivalent to that in a fourth position corresponding to the amino- or nitro-group in nitroaniline. The fifth and sixth positions were attacked in a similar fashion.

One of the nitrophenols belongs to the same series as salicylic acid. A bromine atom and an additional nitro-group can be introduced into this nitrophenol, with the result that the product is identical with that obtained by substituting two nitro-groups for two atoms of hydrogen in bromophenol and thus bromonitro-*nitrophenol*, $C_6H_2 \cdot NO_2 \cdot Br \cdot OH \cdot NO_2$, is identical with dinitro-*bromophenol*, $C_6H_2 \cdot NO_2 \cdot NO_2 \cdot OH \cdot Br$, which signifies that in nitrophenol there are two positions of equal value and symmetrical one with the other in respect of the hydroxyl. There are therefore five equivalent positions. Granted the existence of two symmetrical positions and imagining a plane drawn at right angles through the centre of these two positions, the molecule will be divided into two symmetrical halves, which implies the existence of a second symmetrical pair and it may be therefore concluded that the six positions occupied by hydrogen in the molecule of benzene are of equal value.

Unfortunately, the publication in which this paper appeared was little known to the chemical world, and it was only later that its full significance was realised and its conclusions accepted. Meanwhile, as already stated, the confusion which reigned on the subject of orientation continued to grow.

Whilst at Palermo Körner sent a paper to the Academie des

Sciences on the "Synthesis of a base isomeric with Toluidine," which he obtained by nitrating and reducing *p*-bromotoluene. The paper is interesting from the fact that in it he proposes the formula for pyridine, which is now adopted. His reference to this formula was, however, suppressed in the paper sent to the Academie, probably from its purely theoretical nature, but was afterwards published (1869) as a note in the *Giornale di Scienze Naturali ed Economiche.*

We will leave for a moment Körner's experimental work in order to take up the thread of his subsequent career.

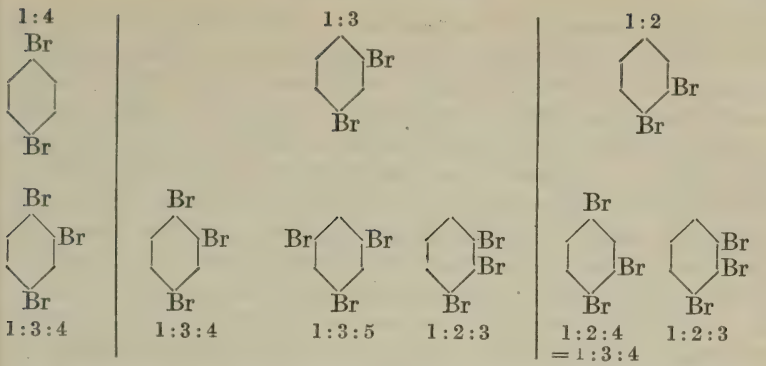
In 1870 the "Scuola Superiore di Agricoltura" was founded at Milan and Körner was elected to the chair of organic chemistry, where he continued with his usual energy to prosecute his experimental studies. In 1874 his classical memoir on "Studi sull' Isomeria delle cose dette Sostanze Aromaticee a shi atomi di carbonio" appeared in the *Gazzetta Chimica Italiana*, in which is collected a mass of new material, the preparation of which had occupied him during the preceding five years.

He begins by explaining the weak points in the views of previous observers on orientation and shows that the only satisfactory method is the one outlined in his paper of 1867.

"For more than six years," he says, "a number of distinguished chemists have occupied themselves with the study of isomerism of the so-called aromatic compounds and still continue to do so. Nevertheless it is a curious fact that no definite solution has up to the present been reached." Further he says: "The most certain method I still believe to be the one suggested seven years ago in my first work on this subject, namely, the transformation of the three isomeric di-derivatives into the isomeric tri-derivatives."

He suggests then the utilisation of the three dibromobenzenes as affording the fewest experimental difficulties.

"The equivalence of the six positions of hydrogen in benzene being granted, it suffices to prepare any complete series of trisubstituted derivatives with these three compounds and to study their relation and in this way an unequivocal solution of the problem will be attained. Thus, by preparing the three possible tribromobenzenes from the dibromobenzenes and discovering for each one of them how many and which of the tribromobenzenes can be prepared or, *vice versa*, finding from the latter to which of the dibromobenzenes it gives rise, a direct and definite method will be afforded for determining the structure of both the di- and tribromobenzenes according to the following scheme:



In the same way, it is possible to prepare the six modifications of dibromoaniline and also the six nitrodibromobenzenes."

The principle, as we know, is simple, elegant, and beyond criticism and has never been seriously questioned.

We have only to survey the number and variety of new compounds, new reactions and new and ingenious devices for obtaining the same substance by different methods, to realise the amount of patient and careful work and experimental skill which this truly classical research entailed.

As his fellow-worker and biographer, Professor Menozzi, has said, "the work suffices to raise Körner to a distinguished position among the great chemists."

In addition to devising a method of orientation independent of any speculation, Körner was able to lay down certain rules of substitution, which possess, not only a scientific interest, but one of great practical value. Putting it very briefly, he showed that if the halogens or nitric acid act on the halogen derivatives of benzene or on aniline, phenol, or toluene so that one atom of hydrogen is substituted, the principal product is the 1 : 4-derivative and, as a secondary product, the 1 : 2-derivative, and the more violent the reaction the larger the quantity of the latter. Where the original group is CO_2H, NO_2, or SO_3H, the principal derivative is a 1 : 3-compound and at the same time a certain amount of 1 : 2- and occasionally 1 : 4-derivative is produced.

If sulphuric acid is allowed to act on the members of the above series, the product is mainly the 1 : 3-derivative with smaller and variable quantities of the 1 : 2-derivative.

At the end of the paper Körner discusses Kekulé's formula for benzene with the alternate double linkages. He shows that the simultaneous formation of 1 : 2- and 1 : 4-derivatives in certain cases and of 1 : 3-derivatives in others cannot be explained by

Kekulé's formula. He proposes one which had already been indicated in a former paper and resembles that of Claus inasmuch as each atom of carbon is linked with three others. This arrangement presupposes the twelve atoms to be disposed in four parallel planes; in each of the outer planes are three atoms of hydrogen 1, 3, 5 and 2, 4, 6 and in each of the inner planes three atoms of carbon. This arrangement affords the maximum symmetry, represents absolute equivalence of the hydrogen atoms and the three cases of isomerism among the di-derivatives.

Besides his work on the constitution of benzene, to which he devoted the greater part of his time and thought, his deep interest in botany led him to the study of many vegetable substances. Between the years 1875 and 1895 he published a series of papers dealing with products of the vegetable kingdom such as the constitution of veratric acid and veratrole, the conversion of aspartic into fumaric acid, on two acids isomeric with vanillic acid, on caffeic acid from cinchona cuprein, on the alkaloids of angustura bark, the constitution of siringina and, in collaboration with Menozzi, on the transformation and synthesis of amino-acids. By the action of methyl iodide on amino-acids in presence of alkali, ammonia is eliminated and an unsaturated acid results: thus aspartic acid gives fumaric acid, alanine is converted into acrylic acid, and leucine into an unsaturated acid containing six carbon atoms. The reverse process was also investigated and carried to a successful issue.

Of Körner's personal character, Professor Angelo Menozzi, a former student and collaborator, has given his impressions in a memorial address, from which the following abstracts have been taken.*

The first thing that strikes one, he says, is that Professor Körner possessed in an eminent degree that quality of the true scientist who devotes himself to the study of science for its own sake, independently of any practical application his discoveries may be found to possess. It so happened that Körner's discoveries, though of scientific importance of the first order, have brought in their train practical results of great value. Körner belongs to that group of scientists who affirm nothing without a rigorous and complete proof and are never in a hurry to publish results. This quality he possessed in an excessive degree. It is certain that it took some pressure on the part of Cannizzaro to persuade Körner to publish his first paper on orientation. Furthermore, the con-

* I wish here to express my indebtedness to my friend Prof. Nasini for the many documents relating to Körner which he was good enough to place at my disposal and also for the photograph which is reproduced here.

stitution of orcin had been established in Körner's laboratory before Tiemann's research appeared in the *Berichte*. The same is true of leucine, the constitution of which was fully known before its publication elsewhere. He recognised this weakness in himself, but as it was of secondary importance to his work, he put it aside as a matter of small significance. Whilst one cannot but regret this excessive caution which led him to control with scrupulous care every conclusion and statement before publication and which may have robbed him of priority in certain discoveries, one cannot but admire a quality which is only too rare among scientific workers of the present day. Körner possessed a keen intuition, which was soon recognised by those with whom he worked. He declared the acid isolated from aspartic acid to be fumaric acid long before its identity was definitely established and the same thing occurred with caffeic acid from angustura.

As a teacher Körner was lucid, profound and effective and his lectures left a lasting impression on the many students who attended his classes.

His method was largely based on experimental demonstrations and Cannizzaro relates that when acting as lecture assistant his arrangement of the experiments was a model of precision and ingenuity. He was skilled in analysis by the dry way and insisted on his students becoming proficient in this method. In the execution of his own researches, in his skill as an experimenter, in the originality of his ideas and in the novelty of his methods he showed a master mind.

He had a passion for preparing his specimens in a state of extreme purity and it is this personal characteristic which is responsible for that remarkable collection of organic substances which is one of the scientific treasures of the School of Agriculture of Milan and is unique in the variety, purity, and beauty of the preparations.

Körner's system of imparting information was essentially practical, for he never forgot that he was teaching in a school of agriculture. If a substance was connected with plant life—he was a passionate lover of flowers and plants and possessed a profound knowledge of plant physiology—he never failed to enlarge upon this relation; similarly any reference to an industrial commodity led to an account of its technical application.

He completed his 75th year in 1914, when, according to the existing rule, he reached the retiring age; but at the instance of the staff of the agricultural school, supported by the Chemical Society of Milan, his services were exceptionally retained until 1922, when for reasons of failing health he resigned his chair at the advanced age of 83.

He lived his last three years in peaceful retirement, happy in his family life and in the visits of his former colleagues and pupils, and passed quietly away on the evening of March 29th, 1925.

Körner was elected honorary member of many Italian and foreign institutions, *viz.*, the Reale Accademia dei Lincei, the Reale Istituto Lombardo di Scienze e Lettere, La Società Italiana delle Scienze, received the honorary doctorate of Oxford, Cambridge, and Giessen, was awarded the Davy medal of the Royal Society and made honorary member of the Royal Institution, of the Chemical Society of London, and of the German Chemical Society. He was enrolled chevalier of the civil order of Savoy for work of scientific merit.

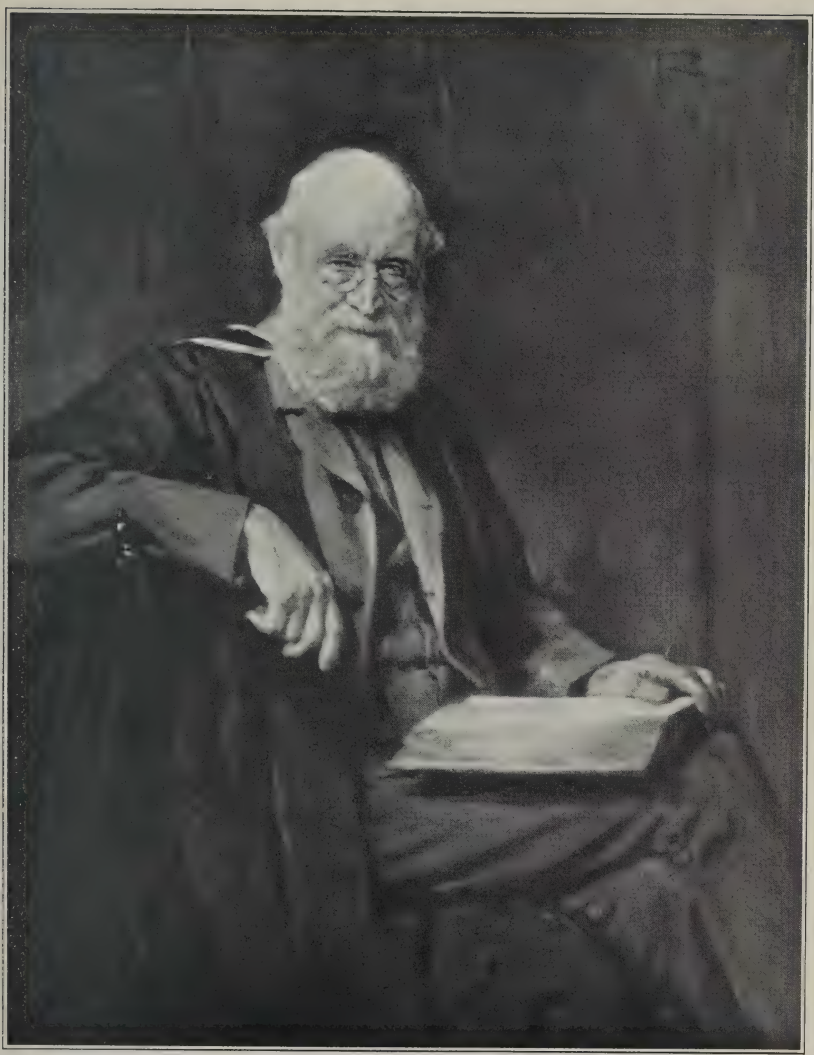
J. B. Cohen.

GEORGE DOWNING LIVEING.

Born December 21st, 1827; Died December 26th, 1924.

By the death of Dr. G. D. Liveing, Professor of Chemistry in the University of Cambridge, at the great age of ninety-seven, the Society loses its oldest member, as he was elected Fellow in 1853. He was the son of Edward Liveing of Nayland, Suffolk. Entering at St. John's College, Cambridge, he was eleventh wrangler in 1850, and, in the following year, he took the Natural Sciences Tripos, then instituted for the first time, and obtained a first class with distinction in Chemistry and Mineralogy. After working in Berlin with Rammelsberg, he was elected to a fellowship at St. John's College in 1853, but, under the Statutes of that period, he had to resign on his marriage in 1860. After acting as Deputy to the Professor of Chemistry (Reverend J. Cumming), he was elected to the Chair in 1861.

It is difficult to convey an idea of the attitude of the University at this period towards the experimental sciences, steeped as it was in the tradition of centuries of classical, mathematical and theological teaching. There was no laboratory instruction for students, although some experiments seem to have been shown in the lectures. Liveing relates how, in 1850, he was attending Mr. Griffin's lectures on Physical Optics and, whilst dealing with the subject of the Fraunhofer lines, the lecturer asked any who wished, to come again later and he would demonstrate their formation. Liveing was the only one in the class who accepted the offer. The apparatus consisted of Wollaston's arrangement for producing a pure spectrum. A prism, a lens, a slit illuminated by an oil lamp, and a screen. Between the lamp and the slit was placed a bottle con-



Sincerely yours
G. D. Livermore

[To face p. 2982.]

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taining some copper turnings on which nitric acid was poured. A series of fine black lines appeared on the screen. The explanation of the formation of the black lines was not given by Bungen and Kirchoff until 1860. Liveing had to fight a long and hard battle to persuade the University that it was their duty to teach the experimental sciences, not by merely showing experiments on a lecture table, but by the only sure method, of making the students perform them themselves.

St. John's College, soon after Liveing took his degree, built him a chemical laboratory and "sowed the first seed towards the growth of a large chemical school," and they allowed him to use this laboratory after he became Professor of Chemistry. The question of providing teaching in experimental sciences had still to be fought out. Plans were drawn up, but when the tenders came in they far exceeded the money the University had to spend. The laboratory proposed for Chemistry, by Professor Willis, consisted of "a building which was capable of standing violent explosions and as uninflammable as possible, containing a series of vaults." Liveing would have none of this, and begged that Chemistry should be left out of the scheme. The result of his action was that Chemistry was only housed in a temporary structure for many years until, in 1887, a laboratory was built on the Pembroke Street site. This building was added to in 1908 and again in 1920, and the department of Physical Chemistry has also taken over the large laboratory vacated by the Engineering department. Altogether the laboratory has accommodation for more than 700 research and ordinary students and is the largest chemical laboratory in the country.

Liveing's contributions to science were on the transmutation of the elements in 1855, and a few papers on geological and chemical subjects. In 1875, Sir James Dewar was appointed Jacksonian Professor of Chemistry, and the two professors almost at once began their researches on the spectroscope, which continued until 1904. These papers have been collected in one large volume and published by the University Press (1915). The work was characterised by its great accuracy, originality, and the patience with which one difficulty after another was overcome, and is now regarded as one of the standard books on the subject.

As a lecturer, Liveing was inspiring to those who had sufficient mathematical ability to follow him. The lectures were illustrated by experiments carefully chosen, and invariably rehearsed, but the experiments not unfrequently failed from his over-anxiety to make them succeed. As the head of a large department, he maintained a stern discipline, and to the younger men he appeared somewhat

unapproachable. Those who knew him intimately, however, were aware that he was the kindest and most liberal of men, and a delightful companion, especially when he was in the mood to tell stories of byegone Cambridge and of his travels, during which he collected specimens of minerals to illustrate his lectures.

Liveing, in addition to his professorial duties, found time to attend with great regularity the magisterial bench and many philanthropic and benevolent committees. For several years he held a commission as captain in the Town and County Rifle Corps; he was also an enthusiastic gardener.

It is not generally known that for the last four years of his life he was actively engaged in an experimental investigation on the absorption of radiant energy by dense substances such as barium sulphate, lead sulphate, cassiterite, litharge, etc. Each vacation he devoted an hour or two every day to working at these problems in the Goldsmiths' metallurgical laboratory, and he spent much time at home in working out his results. This research is far from complete, although it is an amazing testimony to his vigour and perseverance. It was whilst on his way to the laboratory that he met with the accident which caused his death a few weeks later. Liveing resigned his professorship in 1908 and was given the degree of Sc.D.

C. T. Heycock.

ALEXANDER MITCHELL WILLIAMS.

Born September 20th, 1888; Died February 21st, 1925.

The son of a master-baker, Alexander Mitchell Williams was born on September 20th, 1888, at Burntisland in Fifeshire. He attended Burntisland School and later George Watson's College in Edinburgh, where at the age of seventeen he was dux and gold medallist. With the John Welsh mathematical bursary (a foundation of Thomas Carlyle in memory of his father-in-law), Williams entered the University of Edinburgh and had a brilliant record in Mathematics, Physics, and Chemistry. In 1910 he graduated as B.Sc. and as M.A. with first-class honours in Mathematics and Natural Philosophy. During his University period, he gained many scholarships and prizes, being awarded finally an 1851 Exhibition Scholarship which enabled him to proceed to Sweden and work under the guidance of Arrhenius. His chief study in Stockholm was adsorption, a subject which occupied his attention for many years afterwards. On returning to this country he continued research work in the laboratories of Professor Donnan in Liverpool

and in London. In 1915 he was appointed science teacher in Hawick High School, and while there had a serious breakdown in health, from which he never entirely recovered. After temporary service in the Science Department of his old school in Edinburgh, he became a lecturer in the Chemistry Department of Edinburgh University in 1916. Continuing his research work, he graduated as D.Sc. with a thesis on Adsorption. In 1919 he was appointed joint Head of the Physico-chemical Department at the Shirley Institute, Didsbury, the headquarters of the Cotton Industry Research Association. Soon after his appointment he married Miss May Shaw, an Edinburgh lady.

While in Edinburgh, Williams published four valuable papers on adsorption ("Thermodynamics of Adsorption," *Proc. Roy. Soc. Edin.*, 1918, **38**, 23; "The Adsorption Isotherm at Low Concentrations," *ibid.*, p. 48; "The Adsorption of Gases at Low and Moderate Concentrations," Parts I and II, *Proc. Roy. Soc.*, 1919, **96**, *A*, 287; Part III, *ibid.*, p. 298), together with one on "Periodic Precipitation," jointly with Miss M. R. Mackenzie (J., 1920, **117**, 844), and a paper on the "Depolarisation by Oxygen of a Voltaic Cell" (*J. Soc. Chem. Ind.*, 1920, **39**, 285T).

The work of Williams at the Shirley Institute was chiefly concerned with the moisture relations of cotton, and the swelling of cotton cellulose under the influence of alkalis. The results of his researches are published in the *Journal* of the Textile Institute. He showed that the swelling in mercerisation cannot be simply referred to the concentration of the hydroxide ion in the alkali solutions, but is dependent to some extent on a specific effect of the alkali metal. The work so far published may be regarded as a considerable instalment of a systematic account of the nature and reactions of the cotton gel—an account which, when complete, should give to those who use cotton in the textile arts increased powers in manipulating their material. One positive technical success Williams achieved by his discovery of a method for preparing cotton yarn of high insulating power, so making it possible for English firms to compete in a trade which had long been a continental monopoly.

Williams had a first-rate scientific intellect, both critical and constructive. He was a sympathetic and kindly teacher, and his investigations, like all that he did, were carried out with an energy and a fervour of enthusiasm which the state of his bodily health could ill support. A final attack of his insidious malady at the end of 1924 led to his untimely death on February 21st, 1925.

J. W.

GEORGE YOUNG.

BORN SEPTEMBER 9TH, 1867; DIED APRIL 3RD, 1925.

GEORGE YOUNG, the younger son of Archibald Young, surgical instrument maker, was born in Edinburgh on September 9th, 1867. He was educated in Edinburgh at the Collegiate School, George Watson's College, and Minto House. He pursued the study of chemistry at the Polytechnik, Munich, and graduated in 1891 at the University of Erlangen. Soon after returning home, he was appointed demonstrator of chemistry at Firth College, Sheffield, and was afterwards promoted to the lectureship in organic chemistry, a post which he filled with eminent success. Young was an excellent teacher and was most successful in interesting students in research. He contributed many papers on organic chemistry to this *Journal* between the years 1895 and 1905, dealing with the constitution of amidines, the action of ammonias on acetyl urethane, triazoles and their derivatives, and kindred subjects. He was a Fellow of the Chemical Society, of the Institute of Chemistry, and a member of the Society of Chemical Industry.

In his school days, Young was well known in athletic circles as a good sprinter. At Firth College he took a lively interest in the life of the College; he started a students' Chemical Society and at the outbreak of the Boer war he played a vigorous part in organising a company of students, which was attached to the West Yorkshire Royal Engineers. He served with marked success as sergeant-major to the company.

Young severed his connection with the College in 1904, owing to ill health, and moved to London in 1906, where he established a consulting practice. During the Great War he directed his energies to industrial problems with a view to the production of chemicals formerly imported from Germany.

Dr. Young died on April 3rd, 1925, leaving a wife and three daughters to mourn his loss.

W. C. W.

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Veratrylnorhydrohydrastinine, 6′-bromo-, and its salts, and formyl derivative and 6′-nitro- (Haworth and Perkin), 1450.
β-Veratrylpropionic acid, α-cyano-, (Baker and Robinson), 1433.
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Violuric acid, absorption spectra and ionisation of (Morton and Tipping), 2514.
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effect of colloids on the displacement of lead and copper from their salts by (GRAY), 776.
Zinc hydroxide, electrometric precipitation of (BRITTON), 2120.
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FORMULA INDEX.

The following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C_1 group, C_2 group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Salts are placed with the compounds from which they are derived. The chlorides, bromides, iodides, and cyanides of quaternary ammonium bases, however, are registered as group-substances.

C_1 Group.

CH_4 Methane, ignition of mixtures of air with (WHEELER), 14.

CCl_4 Carbon tetrachloride, dielectric constant of (HARRIS), 1065.

1 II

$CHCl_3$ Chloroform, dielectric constant of (HARRIS), 1066.

CH_2O Formaldehyde, vapour pressure of, in aqueous solutions (BLAIR and LEDBURY), 26, 2832.

CH_2O_2 Formic acid, velocity of reaction of bromine with (HAMMICK, HUTCHISON, and SNELL), 2715; action of, on sesquiterpenes (ROBERTSON, KERR, and HENDERSON), 1944.

CH_2Te_2 Ditelluromethane (MORGAN and DREW), 537.

CH_4O Methyl alcohol, preparation of pure (HARTLEY and RAIKES), 524.

CH_5N Methylamine, detection of, in presence of ammonia (VALTON), 40.

CNS Thiocyanogen, action of, on unsaturated compounds (CHALLENGER and BOTT), 1038.

1 III

$CH_2Cl_6Te_2$ Methylenebistelluritrichloride (MORGAN and DREW), 536.

CH_4ON_2 Carbamide, reaction of sodium hypobromite with (DONALD), 2255.

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1 V

CHO_3ClBrS Chlorobromomethanesulphonic acid, optical activity of, and its salts (READ and MCMATH), 1572.

C_2 Group.

C_2H_2 Acetylene, explosion of mixtures of nitrogen and (GARNER and SAUNDERS), 77.

2 II

$C_2H_2O_4$ Oxalic acid, formation of, from ether, and its uranium salts (ROWELL and RUSSELL), 2900; dissociation constants of (BRITTON), 1905; tervalent molybdenum salts (WARDLAW and PARKER), 1311; silver salt, decomposition of (MACDONALD and HINSHELWOOD), 2764.

$C_2H_4Cl_2$ Ethylene dichloride, dielectric constant of (HARRIS), 1066.

C_2H_6O Ethyl alcohol, partial pressures of aqueous solutions of (Dobson), 2866 ; swelling and dispersion of colloids in mixtures of ether and (Mardles), 2940 ; catalysis by alumina of the reaction between ammonia and (Dorrell), 2399.

2 III

$C_2HO_2Cl_3$ Trichloroacetic acid, additive compounds of, with esters (Kendall and Booge), 1771.

$C_2H_3OCl_2$ *s*-Dichlorodimethyl ether, condensation of phenylethylamine with (Short), 269.

2 IV

$C_2H_3O_5ClS$ Chlorosulphoacetic acid, preparation and resolution of, and its salts (Backer and Burgers), 233.

$C_2H_5O_3SNa$ Sodium ethyl sulphoxylate (Vogel and Partington), 1522.

C_3 Group.

$C_3H_4O_4$ Malonic acid, dissociation constants of (Britton), 1906 ; alkaline earth salts, solubilities of (Walker), 62.

$C_3H_6O_2$ Methyl acetate, equilibrium of the hydrolysis of (Burrows), 2723.

$C_3H_6O_3$ Trioxymethylene, action of, on Grignard reagents (Marshall), 2188.

$C_3H_8O_3$ Glycerol, ionic activity of water in aqueous solutions of (Colvin), 2788 ; liquid and vapour phases of aqueous mixtures of (Iyer and Usher), 841.

3 IV

$C_3H_{10}Cl_3SbPd$ Trimethylstibinedichloropalladium hydrochloride (Morgan and Yarsley), 190.

C_4 Group.

$C_4H_4O_2$ Methyl propiolate (Ingold), 1203.

$C_4H_4O_4$ Fumaric acid, Röntgen ray structure of (Yardley), 2207 ; thallous salt (Christie and Menzies), 2370.

Maleic acid, Röntgen ray structure of (Yardley), 2207 ; thallous salt (Christie and Menzies), 2370.

C_4H_6O Acetic anhydride, interaction of tellurium tetrachloride and (Morgan and Drew), 531.

$C_4H_6O_4$ Succinic acid, dissociation constants of (Britton), 1906 ; alkaline earth salts, solubilities of (Walker), 62 ; thallous salt (Christie and Menzies), 2370.

$C_4H_6O_6$ Tartaric acid, dissociation constants of (Britton), 1905 ; thallous salt (Christie and Menzies), 2371.

$C_4H_7N_3$ 2-Amino-4(5)-methylglyoxaline (Burtles and Pyman), 2017.

C_4H_8O Methylvinylcarbinol, resolution and rotation of (Kenyon and Snellgrove), 1174.

$C_4H_8O_2$ Ethyl acetate, effect of salts, sugars, and temperature on solubility of (Glasstone and Pound), 2660.

$C_4H_8S_2$ Triethylene trisulphide, supposed true nature of (Bennett and Berry), 910.

$C_4H_{10}O_2$ Ethyl ether, swelling and dispersion of colloids in mixtures of alcohol and (Mardles), 2940 ; oxidation of, to oxalic acid in presence of uranyl nitrate (Rowell and Russell), 2900.

$C_4H_{10}O_3$ α-Methyl glycerol (Gilchrist and Purves), 2744.

4 III

$C_4H_3O_4N_3$ Violuric acid, absorption spectra and ionisation of (Morton and Tipping), 2514.

$C_4H_6O_4Te$ Tellurodiacetic acid, and its salts (Morgan and Drew), 535.
$C_4H_6O_4Te_2$ Ditellurodiacetic acid (Morgan and Drew), 536.
$C_4H_8OCl_2$ β-Methyl αγ-dichlorohydrin (Gilchrist and Purves), 2743.
$C_4H_8Cl_2Se$ ββ′-Dichlorodiethyl selenide (Bell and Gibson), 1882.
$C_4H_8Cl_4Se$ ββ′-Dichlorodiethyl selenide dichloride (Bell and Gibson), 1880.
$C_4H_8Br_2Se$ ββ′-Dibromodiethyl selenide (Bell and Gibson), 1883.
$C_4H_8Br_4Se$ ββ′-Dibromodiethyl selenide dibromide (Bell and Gibson), 1881.
$C_4H_{11}O_2P$ Diethylphosphinic acid, silver salt of (Collie), 964.

4 IV

$C_4H_5O_2N_3S$ Nitrothiol-2-methylglyoxaline, and its ammonium salt (Bhagwat and Pyman), 1835.
$C_4H_5O_3NCl_2$ Ethyl dichloronitroacetate (Macbeth and Traill), 895.
$C_4H_5O_4NBr_2$ Ethyl dibromonitroacetate (Macbeth and Traill), 896.
$C_4H_6O_4Cl_2Te$ Dichlorotelluridiacetic acid (Morgan and Drew), 534.
$C_4H_7OCl_3Te$ Tellurium methylethylketone trichloride (Morgan and Elvins), 2628.
$C_4H_8Cl_2Br_2Se$ ββ′-Dibromodiethyl selenide dichloride (Bell and Gibson), 1883.
ββ′-Dichlorodiethyl selenide dibromide (Bell and Gibson), 1883.
$C_4H_9O_4N_2Cl$ Ammonio-derivative of ethyl chloronitroacetate (Macbeth and Traill), 895, 1122.
$C_4H_9O_4N_2Br$ Ammonio-derivative of ethyl bromonitroacetate (Macbeth and Traill), 896.
C_4H_9ClSHg *iso*Butyl mercaptan mercurichloride (Birch and Norris), 905.
$C_4H_{10}O_4N_3Cl$ Ethyl chloronitroacetate hydrazide (Macbeth and Traill), 1122.
$C_4H_{10}Cl_2S_2Cd$ Dimethyldithiolethylene cadmium chloride (Morgan, Carter, and Harrison), 1922.
$C_4H_{10}Cl_2S_2Zn$ Dimethyldithiolethylene zinc chloride (Morgan, Carter, and Harrison), 1921.
$C_4H_{10}Br_2S_2Cd$ Dimethyldithiolethylene cadmium bromide (Morgan, Carter, and Harrison), 1922.
$C_4H_{10}I_2S_2Zn$ Dimethyldithiolethylene zinc iodide (Morgan, Carter, and Harrison), 1921.

4 V

$C_4H_5O_4NClBr$ Ethyl chlorobromonitroacetate (Macbeth and Traill), 896.

C_5 Group.

C_5H_5N Pyridine, distribution of, between water and benzene (Woodman and Corbet), 2461.
$C_5H_9N_3$ 2-Amino-4:5-dimethylglyoxaline, and its salts (Burtles and Pyman), 2015.
$C_5H_{10}O$ Ethylvinylcarbinol, resolution and rotation of (Kenyon and Snellgrove), 1175.
$C_5H_{10}O_5$ Arabinose, constitution of (Hirst and Robertson), 358.
$C_5H_{10}S$ Pentamethylene sulphide, and its salts (Thierry), 2758.
$C_5H_{12}O_3$ αβ-Dimethylglycerol (Gilchrist and Purves), 2743.

5 III

$C_5H_3O_5N_3$ 3:5-Dinitro-4-pyridone (Crowe), 2029.
$C_5H_4O_3N_2$ 3-Nitro-4-pyridone (Crowe), 2028.
$C_5H_5O_3N_3$ 3-Nitro-5-amino-4-pyridone, and its hydrochloride (Crowe), 2029.
$C_5H_5O_4I$ 1-Iodo*cyclo*propane-1:2-dicarboxylic acid (Ing and Perkin), 2394.
$C_5H_6ON_2$ 3-Amino-4-pyridone, and its salts (Crowe), 2029.

$C_5H_7O_2N_3$ Nitro-1:2-dimethylglyoxalines, and their salts (Bhagwat and Pyman), 1833.

$C_5H_7O_4K$ Potassium ethyl malonate, electrolysis of (Robertson), 2057.

$C_5H_8N_2S$ 2-Methylamino-4-methylthiazole, and its hydrochloride (Burtles, Pyman, and Roylance), 588.

2-Thioldimethylglyoxalines (Burtles, Pyman, and Roylance), 586.

$C_5H_{10}O_2N_2$ Glutardialdoxime, preparation of (Shaw), 215.

Malonmonoethylamide (West), 750.

$C_5H_{11}IS$ Tetramethylene sulphide methiodide (Thierry), 2758.

$C_5H_{13}O_4N_3$ Hydrazine derivative of ethyl α-nitropropionate (Macbeth and Traill), 897.

5 IV

$C_5H_8O_4NCl$ Ethyl α-chloronitropropionate (Macbeth and Traill), 896.

$C_5H_8O_4NBr$ Ethyl α-bromonitropropionate (Macbeth and Traill), 897.

$C_5H_9OCl_3Te$ Tellurium diethylketone trichloride (Morgan and Elvins), 2629.

$C_5H_9O_2N_2Br$ Bromomalonmonoethylamide (West), 751.

C_6 Group.

C_6H_6 Benzene, dielectric constant of (Harris), 1065 ; cryoscopy with (Jones and Bury), 1947.

6 II

$C_6H_4O_2$ *p*-Benzoquinone, preparation of (Craven and Duncan), 1489.

$C_6H_4O_6$ 3:5-Dinitrocatechol, colorimetric dissociation constants of (Laxton, Prideaux, and Radford), 2499.

4:6-Dinitroresorcinol, colorimetric dissociation constants of (Laxton, Prideaux, and Radford), 2499.

C_6H_6O Phenol, surface tension of aqueous solutions of (Goard and Rideal), 780, 1668 ; molecular condition of, in benzene (Philip and Clark), 1274 ; effect of salts on the equilibrium and critical solution temperature of, in water (Carrington, Hickson, and Patterson), 2544 ; equilibrium of salicylic acid, water, and (Bailey), 1951.

$C_6H_6O_3$ *cis*-1-Methyl*cyclo*propane-1-2-dicarboxylactone (Ingold), 398.

Phloroglucinol, absorption spectra of (Morton and Rogers), 2700.

$C_6H_6O_4$ Phthalic acid, thallous salt (Christie and Menzies), 2370.

C_6H_7N Aniline, physical properties of, and its aqueous solutions (Applebey and Davies), 1836.

$C_6H_8O_4$ αγ-Dialdehydopropane-β-carboxylic acid (Perkin and Pink), 194.

Hydroxy-α-methylglutarolactones, and their salts (Ingold), 394.

cis- and *trans*-1-Methyl*cyclo*propane-1:2-dicarboxylic acids, and their salts (Ingold), 396.

$C_6H_{10}O_3$ Ethyl acetoacetate, interaction of *o*-hydroxydistyryl ketones and (Heilbron, Forster, and Whitworth), 2159.

$C_6H_{10}O_5$ Dextrin, constitution of (Irvine and Oldham), 2914.

Hydroxy-α-methylglutaric acids, and their salts (Ingold), 394.

Methylitamalic acid, barium salt (Ingold), 397.

$C_6H_{12}O$ *n*-Propylvinylcarbinol, resolution and rotation of (Kenyon and Snellgrove), 1176.

$C_6H_{12}O_6$ Dextrose, dissociation constant of (Britton), 1902.

$C_6H_{12}S_2$ Hexamethylene disulphide (Bennett and Hock), 2676.

$C_6H_{14}O_3$ Trimethyl glycerol (Gilchrist and Purves), 2744.

$C_6H_{14}S$ *iso*Propylmercaptan *n*-propyl ether (Birch and Norris), 904.

$C_6H_{15}P$ Triethylphosphine, preparation and reactions of (Collie), 964.

6 III

$C_6H_3O_{12}Al$ Aluminioxalic acid, salts of, with optically active bases (Child, Roberts, and Turner), 2971.

$C_6H_3O_{12}Sb$ Antimonoxalic acid, potassium salt (Holmes and Turner), 1753.

$C_6H_3Cl_3S$ 2:5-Dichlorophenylsulphur chloride (Miller and Smiles), 230.

$C_6H_3FeN_6$ Hydroferricyanic acid, potassium salt, oxidation of carbohydrates by (Knecht and Hibbert), 2854.

C_6H_4ClAs *p*-Chlorophenyldichloroarsine (Hunt and Turner), 2671.

C_6H_5ON Nitrosobenzene, bromination and nitration of (Ingold), 515.

$C_6H_5O_2N$ Nitrobenzene, dielectric constant of (Harris), 1067; cryoscopy with (Brown), 345.

$C_6H_6O_3Ge$ Phenylgermanonic acid (Morgan and Drew), 1764.

$C_6H_6N_2Br_2$ 2:4-Dibromophenylhydrazine, preparation of (Humphries and Evans), 1676.

$C_6H_9O_3N$ β-Ethylcarbonatopropionitrile (Chapman and Stephen), 888.

$C_6H_{11}ON$ α-Ethylcrotonamides (Newbery), 301.

Methylpentenoic amides (Kon and Linstead), 623.

$C_6H_{11}O_3N$ Methoxymethylanthranilic acids (Heilbron, Kitchen, Parkes, and Sutton), 2173.

$C_6H_{12}O_2N_2$ Malonmono*iso*propylamide (West), 750.

$C_6H_{12}O_3S$ *cyclo*Hexanesulphonic acid, salts of (Kolker and Lapworth), 312.

$C_6H_{12}Cl_2S$ γγ′-Dichlorodipropyl sulphide, and its platinic chloride additive compound (Bennett and Hock), 2674.

$C_6H_{13}ClS$ Pentamethylenemethylsulphonium chloride (Thierry), 2759.

6 IV

$C_6H_2O_7N_3Cl$ 3-Chloro-2:5:6-trinitrophenol (Hodgson and Moore), 1603.

C_6H_4OClAs *p*-Chlorophenylarsenious oxide (Hunt and Turner), 2671.

C_6H_4OBrAs *p*-Bromophenylarsenious oxide (Hunt and Turner), 2670.

$C_6H_4O_2NBr$ 3-Bromo-*p*-benzoquinone-4-oxime (Hodgson and Moore), 2261.

Bromonitrosophenols (Hodgson and Moore), 2261.

$C_6H_4O_2NI$ 3-Iodo-*p*-benzoquinone-4-oxime (Hodgson and Moore), 2262.

2-Iodo-4-nitrosophenol (Hodgson and Moore), 2264.

$C_6H_4O_3NCl$ 3-Chloro-2-nitrophenol, and its silver salt (Hodgson and Moore), 1600.

$C_6H_4O_3NBr$ 3-Bromo-4-nitrophenol (Hodgson and Moore), 2262.

$C_6H_4O_3NI$ 3-Iodo-4-nitrophenol (Hodgson and Moore), 2263.

$C_6H_4Cl_2BrAs$ *p*-Bromophenyldichloroarsine (Hunt and Turner), 2670.

C_6H_6ONBr *p*-Bromophenylhydroxylamine, preparation of (Haworth and Lapworth), 2970.

$C_6H_{10}O_2N_2Te$ 2-Methyl*cyclo*telluropentane-3:5-dione dioxime (Morgan and Kellett), 2621.

$C_6H_{10}O_2N_3I$ 4(5)-Nitrotrimethylglyoxalinium iodides (Bhagwat and Pyman) 1834.

$C_6H_{10}O_2Cl_2Te$ Tellurium bisacetone dichloride (Morgan and Elvins), 2628.

$C_6H_{10}O_4NCl$ Ethyl α-chloronitrobutyrate (Macbeth and Traill), 897.

$C_6H_{10}O_4NBr$ Ethyl α-bromonitrobutyrate (Macbeth and Traill), 897.

$C_6H_{11}ONBr_2$ αβ-Dibromo-α-ethylbutyramides (Newbery), 304.

$C_6H_{11}OCl_3Te$ Tellurium pinacolin trichloride (Morgan and Elvins), 2630.

$C_6H_{11}O_2N_2Br$ Bromomalonmono*iso*propylamide (West), 752.

$C_6H_{12}O_2Cl_2S$ γγ′-Dichlorodipropylsulphone (Bennett and Hock), 2675.

$C_6H_{12}Cl_2Br_2S$ γγ′-Dichlorodipropyl sulphide dibromide (Bennett and Hock), 2674.

$C_6H_{14}O_2S_2Hg$ γ-Hydroxypropyl mercaptan mercaptide (Bennett and Hock), 2673.

$C_6H_{18}Cl_2Sb_2Pd$ Bistrimethylstibinedichloropalladium (Morgan and Yarsley), 190.

$C_6H_{18}Cl_2Sb_2Pt$ Bistrimethylstibinedichloroplatinum (Morgan and Yarsley), 188.

6 V

$C_6H_3O_2Cl_2IS$ 2:5-Dichlorobenzenesulphonyl iodide (Gibson, Miller, and Smiles), 1823.

C_7 Group.

C_7H_8 Toluene, catalytic chlorination of (O. and C. A. Silberrad and Parke), 1724; mercuration of (Coffey), 1029.

7 II

$C_7H_6O_2$ Benzoic acid, periodic crystallisation of (Hedges and Myers), 2434.

$C_7H_6O_3$ Salicylic acid, heat of combustion of (Berner), 2747; equilibrium of phenol, water, and (Bailey), 1951.

$C_7H_8O_2$ Resorcinol methyl ether, thallous salt (Christie and Menzies), 2373.

$C_7H_8O_4$ Heptodilactone (Bennett), 1277.

3-Methoxy-3-methyl*cyclo*propane-1:2-dicarboxylic anhydride (Goss, Ingold, and Thorpe), 468.

Methyl hydrogen 3-methyl-Δ^2-*cyclo*propene-1:2-dicarboxylate (Goss, Ingold, and Thorpe), 467.

$C_7H_8O_6$ αγ-Dialdehydopropane-ββ-dicarboxylic acid (Perkin and Pink), 193.

$C_7H_{10}O_6$ *as*-Dimethylcarboxysuccinic acid (Ingold), 473.

$C_7H_{10}N_2$ 3-Amino-2:6-lutidine, and its hydrochloride (Gulland and Robinson), 1495.

$C_7H_{12}O$ Methyl αγ-dimethoxyacetoacetate (Pratt and Robinson), 169.

$C_7H_{12}O_2$ ββ-Dimethyl-α-ethylacrylic acid (Kon, Smith, and Thorpe), 572.

Ethylpentenoic acids (Kon and Linstead), 621.

$C_7H_{12}O_4$ Diethyl malonate, addition of, to esters (Wayne and Cohen), 450.

$C_7H_{14}O$ *n*-Butylvinylcarbinol, resolution and rotation of (Kenyon and Snellgrove), 1177.

$C_7H_{15}I$ Triethylcarbinyl iodide (Morgan, Carter, and Duck), 1253.

7 III

$C_7H_5O_2Br$ Bromohydroxybenzaldehydes (Hodgson and Beard), 878.

$C_7H_5O_2Li$ Lithium salicylaldehyde ($+2H_2O$) (Sidgwick and Brewer), 2385.

$C_7H_5O_2Na$ Sodium salicylaldehyde ($+2H_2O$) (Sidgwick and Brewer), 2385.

$C_7H_5O_6N_3$ Trinitrotoluene, equilibrium of naphthalene and, in nitrobenzene (Brown), 345.

$C_7H_5O_7N_3$ Trinitroanisole, alcoholysis of (Brady and Horton), 2230.

$C_7H_6O_4N_2$ Nitrohydroxybenzaldoximes (Hodgson and Beard), 879.

C_7H_7OBr 2-Bromo-*m*-cresol, preparation of (Hodgson and Beard), 498.

Phenacyl bromide, condensation reactions of (R. M. and J. N. Rây), 2721.

C_7H_7OTl Thallous *m*-tolyloxide (Christie and Menzies), 2373.

$C_7H_7O_2N$ *o*-Nitrotoluene, dielectric constant of (Harris), 1067.

$C_7H_8O_2N_2$ Nitrobenzylamines, and their salts (Holmes and Ingold), 1812.

C_7H_9ON 2-Amino-*m*-cresol, preparation of (Hodgson and Beard), 498.

$C_7H_9O_2N$ 3:4-Dihydroxybenzylamine (Jones and Pyman), 2596.

$C_7H_9O_4Br$ Methyl 1-bromo*cyclo*propane-1:2-dicarboxylate (Ing and Perkin), 2396.

$C_7H_9N_2Cl$ 5-Chloro-2-methyl-*p*-phenylenediamine (Kenner, Tod, and Witham), 2347.
$C_7H_{10}O_4Cl_2$ Di-β-chloroethyl malonate (Bennett), 1278.
$C_7H_{10}O_4Br_2$ Methyl αα′-dibromoglutarates (Ing and Perkin), 2393.
$C_7H_{10}O_4I_2$ Methyl αα′-di-iodoglutarate (Ing and Perkin), 2393.
$C_7H_{11}ON_3$ 2-Acetylamino-4:5-dimethylglyoxaline (Burtles and Pyman), 2016.
$C_7H_{12}O_2N_2$ α-Ethylcrotonylcarbamides (Newbery), 300.
$C_7H_{12}N_2S$ 2-Ethylthiol-1:4-dimethylglyoxaline, salts of (Burtles, Pyman, and Roylance), 588.
$C_7H_{13}ON$ Amides of ethylpentenoic acids (Kon and Linstead), 621.
$C_7H_{13}O_5I$ Methylglucoside 6-iodohydrin (Oldham), 2844.
$C_7H_{13}O_8N$ Methylglucoside 6-nitrate (Oldham), 2844.
$C_7H_{14}O_2N_2$ Malonmono*iso*butylamide (West), 750.
$C_7H_{17}O_2N$ α-Aminopropionacetal (Burtles, Pyman, and Roylance), 586.

7 IV

$C_7H_3O_2NCl_4$ 2:3:4:6-Tetrachloro-3-nitrotoluene (Silberrad), 2683.
$C_7H_5O_2NBr_2$ 4:6-Dibromo-3-hydroxybenzaldoxime (Hodgson and Beard), 880.
$C_7H_5O_3N_2Cl$ 2-Chloro-5-nitrobenzaldoximes (Brady and Bishop), 1361.
$C_7H_5O_3Cl_2S$ 4-Chloroanisole-2-sulphonyl chloride (Gauntlett and Smiles), 2745.
$C_7H_5O_4N_2Cl$ 4-Chloro-2:3-dinitrotoluene (Kenner, Tod, and Witham), 2348.
$C_7H_5O_5N_2Na$ Sodium dinitro-*o*-tolyl oxide (Gibson), 45.
C_7H_6ONBr *o*-Bromo-β-benzaldoxime (Brady, Cosson, and Roper), 2430.
$C_7H_6O_2NBr$ Bromohydroxybenzaldoximes (Hodgson and Beard), 879.
$C_7H_6O_2Cl_2S$ 2:5-Dichlorophenylmethylsulphone (Miller and Smiles), 231.
$C_7H_6O_3NCl$ 3-Chloro-2-nitrophenol methyl ether (Hodgson and Moore), 1601.
$C_7H_6O_3NNa$ Sodium nitro-*o*-tolyl oxides (Gibson), 45.
C_7H_7OClS 4-Chloroanisole-2-mercaptan (Gauntlett and Smiles), 2746.
$C_7H_7O_2N_2Cl$ Chloronitrotoluidines (Kenner, Tod, and Witham), 2346.
$C_7H_7O_2ClS$ 4-Chlorophenylmethylsulphone (Miller and Smiles), 231.
$C_7H_7O_2Cl_3Te$ 2-Hydroxy-1-methoxyphenyl-4-telluritrichloride (Morgan and Drew), 2314.
$C_7H_7O_2BrS$ 3- and 4-Bromophenylmethylsulphones (Twist and Smiles), 1252.
$C_7H_7O_3ClS$ 4-Chloroanisole-2-sulphinic acid (Gauntlett and Smiles), 2746.
$C_7H_7O_4NS$ 3-Nitrophenylmethylsulphone (Twist and Smiles), 1250.
$C_7H_7O_4ClS_2$ *m*-Chlorosulphonylphenylmethylsulphone (Twist and Smiles), 1251.
C_7H_7BrIAs *p*-Bromophenylmethyliodoarsine (Hunt and Turner), 2670.
C_7H_8ONBr 4-Bromo-*m*-anisidine (Griffith and Hope), 994.
$C_7H_{10}O_6NCl$ Ethyl chloronitromalonate (Macbeth and Traill), 1121.
$C_7H_{12}O_2N_2Br_2$ αβ-Dibromo-α-ethylbutyrylcarbamides (Newbery), 305.
$C_7H_{12}O_2N_2Te$ 2:6-Dimethyl*cyclo*telluropentane-3:5-dionedioxime (Morgan and Taylor), 799.
$C_7H_{12}O_2Cl_4Te_2$ Methylenebistelluriacetone dichloride (Morgan and Drew), 537.
$C_7H_{13}OCl_3Te$ Tellurium di-*n*-propylketone trichloride (Morgan and Elvins), 2629.
$C_7H_{13}O_2N_2Br$ α-Bromo-α-ethylbutyrylcarbamide, action of alkalis on (Newbery), 295.
β-Bromo-α-ethylbutyrylcarbamide (Newbery), 305.
Bromomalonmono*iso*butylamide (West), 751.
$C_7H_{14}ON_2S$ 2-Methylamino-5-ethoxy-4-methyl-4:5-dihydrothiazole, and its salts (Burtles, Pyman, and Roylance), 586.

7 V

$C_7H_4NClBr_2S$ Chlorobenzthiazole dibromide (Hunter), 1488.

$C_7H_7ONClBr$ *o*-Bromo-α-benzaldoxime hydrochloride (Brady, Cosson, and Roper), 2430.

$C_7H_7O_4ClSNa$ 4-Chloroanisole-2-sulphonic acid, sodium salt (Gauntlett and Smiles), 2745.

$C_7H_{15}Cl_2I_3SHg$ Dichlorodipropylmethylsulphonium mercuri-iodide (Bennett and Hock), 2675.

C_8 Group.

$C_8H_6O_4$ *m*-Aldehydophenyl carbonate, nitration of (Mason), 1195.

$C_8H_8O_3$ Vanillin, thallous salt (Christie and Menzies), 2373.

$C_8H_8O_7$ Diacetyltartaric anhydride, mutarotation of (Austin and Park), 1926.

$C_8H_{10}O_4$ Ethyl hydrogen 3-methyl-Δ^2-*cyclo*propene-1:2-dicarboxylate (Goss, Ingold, and Thorpe), 468.

$C_8H_{10}O_8$ Diacetyltartaric acid, rotatory dispersion of (Austin and Park), 1926.

$C_8H_{11}N$ Phenylethylamine, condensation of *s*-dichloromethyl ether with (Short), 269.

l-Phenylethylamine, aluminioxalate of (Child, Roberts, and Turner), 2972.

$C_8H_{14}O_2$ 3-Methyldipropionylmethane, and its copper salt (Morgan and Taylor), 799.

$C_8H_{14}O_5$ Ethyl αγ-dimethoxyacetoacetate (Pratt and Robinson), 168.

Ethyl β-ethylcarbonatopropionate (Chapman and Stephen), 889.

Acid, from sodium ethoxide and ethyl α-chloro-γ-methylglutarate (Goss and Ingold), 2779.

$C_8H_{14}O_6$ Trimethylarabonolactones (Pryde, Hirst, and Humphreys), 354.

$C_8H_{16}O_5$ Trimethyl γ-arabinose (Baker and Haworth), 368.

8 III

$C_8H_5O_2N$ Isatin, absorption spectra of (Morton and Rogers), 2698.

$C_8H_6O_2Br_2$ 4:6-Dibromo-3-methoxybenzaldehyde (Hodgson and Beard), 879.

$C_8H_6Cl_3As$ α-Chlorostyryldichloroarsine (Hunt and Turner), 998.

$C_8H_7O_2N$ 1-Hydroxy-2:3-benzoxazine (Griffiths and Ingold), 1704.

1-Hydroxy*iso*indole-2-oxide (Griffiths and Ingold), 1706.

$C_8H_7O_3Br$ 3-Bromo-2-hydroxy-5-methoxybenzaldehyde (Rubenstein), 2001.

Bromomethoxybenzoic acids (Hodgson and Beard), 880.

$C_8H_7O_3Li$ Lithium methyl salicylate ($+ 2H_2O$) (Sidgwick and Brewer), 2384.

$C_8H_7O_5N$ 3-Nitro-2-hydroxy-5-methoxybenzaldehyde (Rubenstein), 2000.

5-Nitro-2-hydroxy-4-methoxybenzaldehyde (Rao, Srikantia, and Iyengar), 557.

$C_8H_7O_7N_3$ Trinitrophenetole, alcoholysis of (Brady and Horton), 2230.

$C_8H_7Cl_2As$ Phenyl-β-chlorovinylchloroarsine (Hunt and Turner), 997.

$C_8H_8O_2Se$ Phenylselenoglycollic acid (Morgan and Porritt), 1757.

$C_8H_8O_3N$ Phthalamic acid, ammonium salt (Chapman and Stephen), 1793.

$C_8H_8O_3N_2$ 3-Nitro-4-methylbenzaldoximes (Brady, Cosson, and Roper), 2432.

C_8H_9OBr 2-Bromoanisic acid (Griffith and Hope), 993.

$C_8H_{10}O_2N_2$ 3-Amino-2:6-dimethyl*iso*nicotinic acid, and its salts (Gulland and Robinson), 1494.

Benzylmethylamines, nitro-, and their hydrochlorides (Holmes and Ingold), 1814.

α-Hydroxybenzylcarbamide, and its salts (Wood and Lilley), 97.

$C_8H_{10}O_2S_2$ *m*-Methylthiolphenylmethylsulphone (Twist and Smiles), 1251.

$C_8H_{10}O_4N_2$ 4-Nitro-2:5-dimethoxyaniline, hydrochloride of (Rubenstein), 2004.

$C_8H_{10}IAs$ *p*-Tolylmethyliodoarsine (Mills and Raper, 2481.

$C_8H_{11}ON$ *α*-Hydroxybenzylmethylamine (Wood and Lilley), 96.

$C_8H_{12}O_2Te$ 2:4:6-Trimethyl*cyclo*telluropentane-3:5-dione (Morgan and Taylor), 800.

$C_8H_{13}O_4Cl$ Methyl *γ*-chloro-*α*-methylglutarate (Ingold), 393.

$C_8H_{13}O_4Br$ Methyl *γ*-bromo-*α*-methylglutarate (Ingold), 393.

$C_8H_{13}O_4I$ Methyl *α*-iodo-*α*-methylglutarate (Ingold), 394.

$C_8H_{14}O_2Br_2$ Ethyl *αε*-dibromopentane-*γ*-carboxylate (Mills and Bains), 2505.

$C_8H_{16}O_2N_2$ Malonmonoethylmono*iso*propylamide (West), 750.

$C_8H_{16}O_5N_2$ Trimethoxyglutardiamide (Hirst and Robertson), 362.

$C_8H_{16}O_{10}N_2$ 2:3:5-Trimethyl glucose 1:6-dinitrate (Oldham), 2841.

$C_8H_{17}O_2N$ *α*-Ethoxy-*α*-ethylbutyramide (Newbery), 307.

$C_8H_{19}O_2N$ *α*-Methylaminopropionacetal (Burtles, Pyman, and Roylance), 586.

8 IV

$C_8H_5O_3NBr_2$ 4:5-Dibromophthalamic acid, and its ammonium salt (Chapman and Stephen), 1794.

$C_8H_6O_2N_2S$ Nitrobenzyl thiocyanates (Footner and Smiles), 2890.

$C_8H_7O_2BrSe$ *p*-Bromophenylselenoglycollic acid (Morgan and Porritt), 1757.

$C_8H_7O_2Br_3Se$ *p*-Bromophenylselenoglycollic acid dibromide (Morgan and Porritt), 1759.

$C_8H_7O_2Br_5Se$ *p*-Bromophenylselenoglycollic acid tetrabromide (Morgan and Porritt), 1759.

$C_8H_7O_3BrSe$ *p*-Bromophenylselenoxyglycollic acid (Morgan and Porritt), 1758.

$C_8H_8ON_2Br_2$ Acetyl-2:4-dibromophenylhydrazine, and its hydrobromide (Humphries and Evans), 1677.

$C_8H_8O_2NBr$ 6-Bromo-3-methoxybenzaldoxime (Hodgson and Beard), 880.

$C_8H_8O_3NCl$ 4-Chloro-6-nitro-*m*-tolyl methyl ether (Kenner, Tod, and Witham), 2348.

$C_8H_8O_3NBr$ 5-Bromo-2-amino-4-methoxybenzoic acid, and its salts (Griffith and Hope), 994.

$C_8H_9ON_2Br$ Acetyl-*p*-bromophenylhydrazine, and its hydrobromide (Humphries and Evans), 1676.

$C_8H_9OCl_3Te$ *p*-Phenetyltelluritrichloride (Morgan and Drew), 2311.

$C_8H_9O_2Cl_3Te$ 1:3-Dimethoxyphenyl-4-telluritrichloride (Morgan and Drew), 2312.

$C_8H_9O_3N_2Cl$ 3-Nitro-4-methyl-*β*-benzaldoximehydrochloride (Brady, Cosson, and Roper), 2432.

$C_8H_9O_3ClS$ 4-Chloroanisole-2-methylsulphone (Gauntlett and Smiles), 2746.

$C_8H_{10}ONCl$ 5-Chloro-2-amino-4-methoxytoluene (Heilbron, Kitchen, Parkes, and Sutton), 2175.

$C_8H_{10}OI_2Te$ *p*-Anisylmethyltelluridi-iodide (Morgan and Drew), 2315.

$C_8H_{12}O_2Cl_2Te$ 2:4:6-Trimethyl*cyclo*telluripentane-3:5-dione 1:1-dichloride (Morgan and Taylor), 800.

$C_8H_{13}O_2NTe$ 2-Methyl-4-ethyl*cyclo*telluropentane-3:5-dione monoxime (Morgan and Kellett), 2622.

$C_8H_{14}O_2N_2Te$ 2-Methyl-4-ethyl*cyclo*telluropentane-3:5-dione dioxime (Morgan and Kellett), 2622.

2:4:6-Trimethyl*cyclo*telluropentane-3:5-dionedioxime (Morgan and Taylor), 800.

$C_8H_{15}O_2N_2Br$ Bromomalonmonoethylmono*iso*propylamide (West), 752.

$C_8H_{20}I_2S_4Cu_2$ Dimethyldithiolethylene cuprous iodide (Morgan, Carter, and Harrison), 1922.

C_9 Group.

C_9H_{20} 3:3-Diethylpentane (Morgan, Carter, and Duck), 1252.

9 II

$C_9H_6O_3$ 4-Aldehydo-1:2-phthalide (Perkin and Stone), 2290.

$C_9H_6O_4$ 4-Carboxy-1:2-phthalide (Perkin and Stone), 2291.

2:4-Dialdehydobenzoic acid (Perkin and Stone), 2292.

$C_9H_6O_5$ 2-Aldehydoterephthalic acid (Perkin and Stone), 2294.

C_9H_8O Cinnamaldehyde, action of, on Grignard reagents (Marshall), 2186.

$C_9H_8O_2$ 4-Methyl-1:2-phthalide (Perkin and Stone), 2285.

$C_9H_8O_3$ Hydroxy-3:4-dihydrocoumarins (Chapman and Stephen), 890.

4-Hydroxymethyl-1:2-phthalide (Perkin and Stone), 2287.

$C_9H_8O_5$ 2-Hydroxymethylterephthalic acid (Perkin and Stone), 2291.

$C_9H_9N_3$ Aminophenylglyoxalines, and their salts (Balaban and King), 2710.

$C_9H_{10}O_2$ 2:4-Dimethylbenzoic acid (Perkin and Stone), 2283.

$C_9H_{10}O_3$ Ethyl acetoacetate, thallous salt (Christie and Menzies), 2372.

Hydroxydimethylbenzoic acids (Perkin and Stone), 2285.

4-Methoxy-3-methylbenzoic acid (Brady, Cosson, and Roper), 2431.

$C_9H_{10}O_4$ *m*-Aldehydophenyl ethyl carbonate, nitration of (Mason), 1195.

2:4-Di(hydroxymethyl)benzoic acid (Perkin and Stone), 2287.

β-2:6-Dihydroxyphenylpropionic acid (Chapman and Stephen), 891.

$C_9H_{10}Br_2$ αγ-Dibromo-β-phenylpropane (Mills and Bains), 2505.

$C_9H_{12}O_2$ Benzyl hydroxyethyl ether (Bennett), 1279.

$C_9H_{12}O_4$ Methyl ethyl 3-methyl-Δ^2-*cyclo*propene-1:2-dicarboxylate (Goss, Ingold, and Thorpe), 468.

Nonodilactone (Bennett), 1278.

$C_9H_{14}O_2$ Acetylmethyl*cyclo*hexanone, beryllium salt (Morgan and Elvins) 2624.

α-Campholytic acid, structure of (Chandrasena, Ingold, and Thorpe), 1677.

1-Methyl*cyclo*hexylidene-4-acetic acid, rotatory dispersion of (Richards and Lowry), 238.

$C_9H_{14}O_3$ 1-Methyl*cyclo*hexan-3-one-1-acetic acid, and its silver salt (Farmer and Ross), 2365.

Lactone, from *Alstonia* bark (Goodson and Henry), 1647.

$C_9H_{14}O_5$ Acid, and its salts, from chenopodium oil (Henry and Paget), 1653.

$C_9H_{16}O_2$ 3-Butylacetylacetones, and their salts (Morgan and Jones), 2618.

Di*iso*butyrylmethane, and its copper salt (Morgan and Taylor), 803.

Ethyl ethylpentenoates (Kon and Linstead), 622.

3-*n*- and -*iso*-Propylpropionylacetones (Morgan and Corby), 2616.

$C_9H_{16}O_3$ β-*iso*Valeryl-α-methylpropionic acid (Jones and Smith), 2536.

$C_9H_{18}O_4$ Ethyl ββ-diethoxypropionate (Ingold), 1203.

$C_9H_{18}O_5$ Trimethyl γ-methylarabinoside (Baker and Haworth), 367.

$C_9H_{18}O_6$ Dimethyl methylglucoside (Irvine and Oldham), 2920.

Glycerolglucoside (Gilchrist and Purves), 2735.

Trimethylglucose, synthesis of (Irvine and Oldham), 2729.

9 III

$C_9H_3OCl_7$ 2:4-Di(trichloromethyl)benzoyl chloride (Perkin and Stone), 2295.

$C_9H_3O_2Cl_5$ 4-Trichloromethyl-1:2-phthalyl chloride (Perkin and Stone), 2296.

$C_9H_4OCl_6$ Pentachloro-2:4-dimethylbenzoyl chlorides (Perkin and Stone), 2293.

$C_9H_4O_2Cl_6$ 2:4-Di(trichloromethyl)benzoic acid (Perkin and Stone), 2296.

$C_9H_5OCl_5$ 2:4-Di(dichloromethyl)benzoyl chloride (Perkin and Stone), 2291.

$C_9H_5O_2Cl_3$ 4-Dichloromethyl-1:2-chlorophthalide (Perkin and Stone), 2292.
$C_9H_6OCl_4$ Trichlorodimethylbenzoyl chloride (Perkin and Stone), 2289.
$C_9H_6O_2Cl_4$ 2:4-Di(dichloromethyl)benzoic acid (Perkin and Stone), 2291.
$C_9H_6N_2Br_2$ 2:5(2:4)-Dibromo-4(5)-phenylglyoxaline (Forsyth and Pyman), 578.
C_9H_7ON Carbostyril, absorption spectra of (Morton and Rogers), 2698.
$C_9H_7ON_6$ 2-Methylpyridine-3:4:6-tricarboxylic acid, thallous salt (Christie and Menzies), 2371.
$C_9H_7OBr_3$ 2:4-Di(bromomethyl)benzoyl bromide (Perkin and Stone), 2286.
$C_9H_7O_2N$ *o*-Methoxybenzoyl cyanide (Marsh and Stephen), 1635.
$C_9H_7O_2Cl$ 4-Chloromethyl-1:2-phthalide (Perkin and Stone), 2289.
$C_9H_7O_2Br$ 4-Bromomethyl-1:2-phthalide (Perkin and Stone), 2287.
$C_9H_7O_3N$ Methylisatoic anhydride (Heilbron, Kitchen, Parkes, and Sutton), 2171.
$C_9H_7O_5N$ 2-Aldehydoterephthalic acid oxime (Perkin and Stone), 2294.
$C_9H_7N_2Br$ Bromophenylglyoxalines, and their salts (Forsyth and Pyman), 576.
$C_9H_8OBr_2$ Bromodimethylbenzoyl bromides (Perkin and Stone), 2284.
$C_9H_8O_2Br_2$ 2:4-Di(bromomethyl)benzoic acid (Perkin and Stone), 2286.
$C_9H_8O_4N_2$ Acetyl-*o*-nitro-*β*-benzaldoxime (Brady and McHugh), 2423.
$C_9H_8O_5N$ Dinitromethoxystyrene (C. K. and E. H. Ingold), 872.
$C_9H_8O_5N_2$ 3-Nitro-2-acetylaminobenzoic acid (Chapman and Stephen), 1795.
$C_9H_8O_6N_2$ 3:5-Dinitro-*o*-tolyl acetate (Gibson), 46.
C_9H_9ON 4-Methoxy-3-methylbenzonitrile (Brady, Cosson, and Roper), 2431.
o-Methylphthalimidine (Griffiths and Ingold), 1708.
C_9H_9OCl 2:4-Dimethylbenzoyl chloride, action of halogens on (Perkin and Stone), 2275.
$C_9H_9O_2N$ 6-Hydroxy-4-keto-1:2:3:4-tetrahydroquinoline (Clemo and Perkin), 2307.
1-Methoxy-2:3-benzoxazine (Griffiths and Ingold), 1704.
Methoxy*iso*indole 2-oxide (Griffiths and Ingold), 1708.
N-Methoxyphthalimidine (Griffiths and Ingold), 1707.
$C_9H_9O_2Cl$ *o*-Acetoxybenzyl chloride (Gray), 1155.
r-*β*-Chlorohydratropic acid, resolution of (McKenzie and Strathern), 86.
$C_9H_9O_2Br$ Bromodimethylbenzoic acid (Perkin and Stone), 2284.
β-Bromo-*β*-phenylpropionic acid, ammonium salt (Senter and Ward), 1849.
$C_9H_9O_3Br$ Bromo-2:5-dimethoxybenzaldehydes (Rubenstein), 2001.
$C_9H_9O_4N$ Nitro-*o*-tolyl acetates (Gibson), 46.
$C_9H_9O_5N$ Nitro-2:5-dimethoxybenzaldehydes (Rubenstein), 2000.
3-Nitro-4-ethoxybenzoic acid (King and Murch), 2645.
Acid, and its salts from oxidation of ethoxylutidine (Collie and Bishop), 963.
$C_9H_{10}O_2N_2$ Methoxy-2-methyl-4-quinazolones (Heilbron, Kitchen, Parkes, and Sutton), 2173.
$C_9H_{10}O_2N_4$ Phthalaldehyde 1-oxime-2-semicarbazone (Griffiths and Ingold), 1704.
$C_9H_{10}O_2Se$ *p*-Tolylselenoglycollic acid (Morgan and Porritt), 1758.
$C_9H_{10}O_3Se$ *p*-Tolylselenoxyglycollic acid (Morgan and Porritt), 1758.
$C_9H_{10}O_5N_2$ Acid, and its silver salt from oxidation of nitroethoxylutidine (Collie and Bishop), 963.
$C_9H_{10}O_6N_2$ Trimethylene glycol mono-2:4-dinitrophenyl ether (Fairbourne and Foster), 2761.
$C_9H_{11}ON$ Hydroxyhydrindamine, chlorobromomethanesulphonates (Read and McMath), 1587.
$C_9H_{11}OCl$ Benzyl chloroethyl ether (Bennett), 1280.

$C_9H_{11}O_2N$ 4-Methoxy-3-methylbenzaldoximes (Brady, Cosson, and Roper), 2431.

$C_9H_{11}O_2Br$ 2:3-Dimethoxybenzyl bromide (Haworth and Perkin), 1437.
3:4-Dimethoxybenzyl bromide (Haworth, Perkin, and Rankin), 1445.

$C_9H_{12}O_2N_2$ Methoxymethylanthranilamides (Heilbron, Kitchen, Parkes, and Sutton), 2174.

$C_9H_{12}O_3N_2$ Nitroethoxylutidine (Collie and Bishop), 962.

$C_9H_{12}O_4N$ 3-Amino-2:5-dimethoxybenzoic acid, and its hydrochloride (Rubenstein), 2002.

$C_9H_{12}O_4Br_2$ Methyl ethyl 2:3-dibromo-3-methyl*cyclo*propane-1:2-dicarboxylate (Goss, Ingold, and Thorpe), 468.

$C_9H_{14}ON_2$ Aminoethoxylutidine, and its salts (Collie and Bishop), 962.

$C_9H_{14}O_2Te$ 4-*iso*Butyl*cyclo*telluropentane-3:5-dione (Morgan and Jones), 2619.
4-*sec.*-Butyl*cyclo*telluropentane-3:5-dione (Morgan and Elvins), 2623.
2-Methyl-4-propyl*cyclo*telluropentane-3:5-diones (Morgan and Corby), 2616.

$C_9H_{14}O_4Br_2$ $\alpha\gamma$-Dibromo-$\beta\beta$-dimethyl-α-ethylglutaric acids (Kon, Smith, and Thorpe), 571.

$C_7H_{16}O_3N_2$ Ethyl hydrazotricarboxylate (Ingold and Weaver), 381.

$C_9H_{17}ON_3$ δ-Ethylhexenone semicarbazones (Kon and Linstead), 818.

$C_9H_{18}O_2N_2$ Malondi*iso*propylamide (West), 750.

$C_9H_{19}ON$ α-*iso*Propyl-*n*-hexoamide (Jones and Pyman), 2597.

9 IV

$C_9H_5ONCl_6$ 2:4-Di(trichloromethyl)benzamide (Perkin and Stone), 2296.

$C_9H_7O_3NBr_2$ 4:5-Dibromo-2-acetylaminobenzoic acid (Chapman and Stephen), 1794.

$C_9H_7O_4N_2Cl$ α-Acetyl-2-chloro-5-nitrobenzaldoxime (Brady and Bishop), 1361.

$C_9H_8O_2NBr$ Acetyl-*o*-bromo-α-benzaldoxime (Brady, Cosson, and Roper), 2429.

$C_9H_9OCl_3Te$ Tellurium phenylethylketone trichloride (Morgan and Elvins), 2631.

$C_9H_9O_3N_2Cl$ Acetylchloronitrotoluidines (Kenner, Tod, and Witham), 2346.

$C_9H_{10}O_2Br_2Se$ *p*-Tolylselenoglycollic acid dibromide (Morgan and Porritt), 1759.

$C_9H_{10}O_2Br_4Se$ *p*-Tolylselenoglycollic acid tetrabromide (Morgan and Porritt), 1759.

$C_9H_{13}OITe$ *p*-Anisyldimethyltelluri-iodide (Morgan and Drew), 2314.

$C_9H_{14}O_2Cl_2Te$ 2-Methyl-4-propyl*cyclo*telluripentane-3:5-dione dichlorides (Morgan and Corby), 2616.

$C_9H_{17}O_2N_2Br$ Bromomalondi*iso*propylamide (West), 751.

$C_9H_{24}O_2Cl_2Te$ 4-*iso*Butyl*cyclo*telluripentane-3:5-dione 1:1-dichloride (Morgan and Jones), 2619.

C_{10} Group.

$C_{10}H_8$ Naphthalene, equilibria of, in nitrobenzene solution (Brown), 345.

$C_{10}H_{16}$ Limonene, action of hydrogen peroxide on (Sword), 1632.
Sylvestrene, occurrence of (Rao and Simonsen), 2494.

$C_{10}H_{18}$ Decahydronaphthalene, isomerism of (Wightman), 1421.

10 II

$C_{10}H_8O_4$ 1:2-Phthalide-4-acetic acid (Perkin and Stone), 2288.

$C_{10}H_{10}O_2$ Benzoylacetone, thallous salt (Christie and Menzies), 2372.

$C_{10}H_{10}O_3$ Phenyl α-methoxy-β-hydroxyvinyl ketone (Malkin and Robinson), 1192.

$C_{10}H_{10}O_4$ *m*-Meconine, preparation and nitration of (Rây and Robinson), 1618.

$C_{10}H_{10}O_4$ Meconines, synthesis of (Edwards, Perkin, and Stoyle), 195.
$C_{10}H_{10}O_5$ 4-Ethylcarbonatobenzoic acid (King and Murch), 2649.
$C_{10}H_{10}N_2$ 2-Phenyl-1-methylglyoxaline, and its salts (Balaban and King), 2714.
$C_{10}H_{11}N$ 1:2-Dihydroquinaldine, synthesis of (Mason), 1032.
$C_{10}H_{12}O$ 2:4-Dimethylacetophenone (Perkin and Stone), 2283.
$C_{10}H_{12}O_2$ Methyl 2:4-dimethylbenzoate (Perkin and Stone), 2284.
$C_{10}H_{12}O_3$ Dimethoxyacetophenones (Pratt and Robinson), 1184.
$C_{10}H_{12}Br$ $\alpha\gamma$-Dibromo-β-phenyl-β-methylpropane (Mills and Bains), 2504.
$C_{10}H_{13}Br$ β-Bromo-α-phenyl-β-methylpropane (Trotman), 94.
$C_{10}H_{14}O_2$ Camphorquinone, rotation of (Lowry and Cutter), 614.
β-Phenyl-β-methylpropane-$\alpha\gamma$-diol (Mills and Bains), 2503.
$C_{10}H_{14}O_4$ 2-Carboxy*bicyclo*-[4,1,0]heptane-1-acetic acid (Baker), 989.
Δ^1-*cyclo*Hexene-1:2-diacetic acid (Baker), 990.
$C_{10}H_{14}O_5$ Anhydro-β-methylpimelic-β-acetic acid (Farmer and Ross), 2364.
1:2-Dihydroxy*cyclo*hexane-1:2-diacetolactone (Baker), 989.
$C_{10}H_{14}N_2$ Nicotine, rotation of (Patterson and Fulton), 2439.
$C_{10}H_{15}Br$ β-Bromo-α-phenyl-β-methylbutane (Trotman), 91.
$C_{10}H_{15}As$ *p*-Tolylmethylethylarsine (Mills and Raper), 2481.
$C_{10}H_{16}O$ Camphor, rotation of (Lowry and Cutter), 612; rotation of halogen derivatives (Cutter, Burgess, and Lowry), 1260.
Tagetone (Jones and Smith), 2538.
$C_{10}H_{16}O_2$ Diethyldihydroresorcinol (Kon and Linstead), 819.
l-2:2:4-Trimethyl-Δ^3-*cyclo*hexene-1-carboxylic acid (Gibson and Simonsen), 1303.
$C_{10}H_{16}O_5$ Ethyl acetylsuccinate, halogenation of (Macbeth and Traill), 1118.
$C_{10}H_{16}O_6$ β-Methylpimelic-β-acetic acid (Farmer and Ross), 2364.
$C_{10}H_{16}N_2$ *cyclo*Pentylideneazine, action of hydrochloric acid on (Perkin and Plant), 1138.
$C_{10}H_{18}O$ Borneol, rotation of (Lowry and Cutter), 614.
$\gamma\eta$-Dimethyl-Δ^α-octen-ϵ-one (Jones and Smith), 2534.
α- and β-Fenchyl alcohols, and their esters, rotatory powers of (Kenyon and Priston), 1472.
Substance, from reduction of tagetone (Jones and Smith), 2538.
$C_{10}H_{18}O_2$ *dl-sec.*-Amylacetylacetone, and its copper salt (Morgan and Elvins), 2623.
$C_{10}H_{18}O_4$ *iso*Propyl-*n*-butylmalonic acid (Jones and Pyman), 2597.
$C_{10}H_{18}O_6$ Tetramethyl galactonolactone (Pryde, Hirst, and Humphreys), 352.
$C_{10}H_{18}O_7$ Methyl arabotrimethoxyglutarate (Hirst and Robinson), 362.
$C_{10}H_{20}O$ $\gamma\eta$-Dimethyl-Δ^α-octen-ϵ-ol (Jones and Smith), 2535.
$C_{10}H_{20}O_6$ Trimethyl methylglucoside (Irvine and Oldham), 2920.
$C_{10}H_{21}N$ *l*-Menthylamine, aluminioxalate of (Child, Roberts, and Turner), 2972.
$C_{10}H_{22}O$ $\gamma\eta$-Dimethyloctan-ϵ-ol (Jones and Smith), 2535.

10 III

$C_{10}H_6O_2Cl_6$ Methyl 2:4-di(trichloromethyl)benzoate (Perkin and Stone), 2296.
$C_{10}H_7OTl$ Thallous α-naphthoxide (Christie and Menzies), 2373.
$C_{10}H_7O_2N$ 4-Cyanomethyl-1:2-phthalide (Perkin and Stone), 2288.
$C_{10}H_7O_4N$ 2-Carboxy-4:5-methylenedioxyphenylacetonitrile (Haworth and Pink), 1370.
4:5-Methylenedioxyhomophthalimide (Haworth and Pink), 1371.

$C_{10}H_8O_2Cl_4$ Methyl 2:4-di(dichloromethyl)benzoate (PERKIN and STONE), 2291.
$C_{10}H_8O_3N_4$ Glyoxalinecarboxynitroanilides, and their salts (BALABAN and KING), 2705.
$C_{10}H_8O_4N_2$ β-6-Nitropiperonylpropionitrile (BAKER and ROBINSON), 1428.
$C_{10}H_8NBr$ 2-Bromo-6-methylquinoline, and its salts (CONOLLY), 2085.
$C_{10}H_9O_2N$ β-Piperonylpropionitrile (BAKER and ROBINSON), 1424.
$C_{10}H_9O_2N_3$ 2-*p*-Nitrophenyl-1-methylglyoxaline, and its salts (BALABAN and KING), 2710.
$C_{10}H_9O_2Li$ Lithium benzoylacetone ($+2H_2O$) (SIDGWICK and BREWER), 2383.
$C_{10}H_9O_2Na$ Sodium benzoylacetone ($+2H_2O$) (SIDGWICK and BREWER), 2383.
$C_{10}H_9O_3N$ Methoxyacetanthranils (HEILBRON, KITCHEN, PARKES, and SUTTON), 2173.
1:2-Phthalide-4-acetamide (PERKIN and STONE), 2288.
$C_{10}H_9O_4N$ Acetyl-3:4-methylenedioxy-α-benzaldoxime (BRADY and MCHUGH), 2422.
Methoxymethylisatoic anhydrides (HEILBRON, KITCHEN, PARKES, and SUTTON), 2174.
$C_{10}H_9O_4Br$ 6-Bromo-4:5-dimethoxyphthalide (RÂY and ROBINSON), 1622.
$C_{10}H_9O_5N$ 4:5-Methylenedioxyhomophthamic acid (HAWORTH and PINK), 1371.
$C_{10}H_9O_6N$ 6-Nitro-4:5-dimethoxyphthalide (RÂY and ROBINSON), 1621.
β-6-Nitropiperonylpropionic acid (BAKER and ROBINSON), 1428.
$C_{10}H_9O_7N$ 3-Nitro-4-ethylcarbonatobenzoic acid (KING and MURCH), 2649.
$C_{10}H_9N_2Br$ 5-Bromo-4-phenyl-1-methylglyoxaline, and its picrate (FORSYTH and PYMAN), 576.
1:4-Di-*p*-bromophenyl-3:6-diphenyl-1:4-dihydro-1:2:4:5-tetrazine (CHATTAWAY and WALKER), 982.
$C_{10}H_9N_4Br$ *p*-Bromobenzeneazomethylglyoxalines (BURTLES and PYMAN), 2016.
$C_{10}H_9Cl_2As$ Phenyl-ββ′-dichlorodivinylarsine (HUNT and TURNER), 997.
$C_{10}H_{10}ON_4$ Glyoxalinecarboxyaminoanilides, and their salts (BALABAN and PYMAN), 2706.
$C_{10}H_{10}O_2Br_2$ Methyl 2:4-di(bromomethyl)benzoate (PERKIN and STONE), 2287.
$C_{10}H_{10}O_4N_2$ Acetyl-3-nitro-4-methyl-α-benzaldoxime (BRADY, COSSON, and ROPER), 2432.
$C_{10}H_{10}O_8N_2$ Glycerol α-mono-3:5-dinitrobenzoate (FAIRBOURNE and FOSTER), 2763.
$C_{10}H_{10}N_2S$ 2-Thiol-1-phenyl-4-methylglyoxaline (BURTLES, PYMAN, and ROYLANCE), 589.
$C_{10}H_{11}ON$ 4-Ketomethyl-1:2:3:4-tetrahydroquinolines (CLEMO and PERKIN), 2303.
$C_{10}H_{11}O_2N$ 6-Methoxy-4-keto-1:2:3:4-tetrahydroquinoline (CLEMO and PERKIN), 2306.
$C_{10}H_{11}O_2Br$ Methyl bromodimethylbenzoates (PERKIN and STONE), 2285.
$C_{10}H_{11}O_4N$ 6-Amino-4:5-dimethoxyphthalide (RÂY and ROBINSON), 1622.
$C_{10}H_{11}O_5N$ 5-Nitro-4-methoxy-2-ethoxybenzaldehyde (RAO, SRIKANTIA, and IYENGAR), 559.
6-Nitro-3-methoxy-2-ethoxybenzaldehyde (RUBENSTEIN), 2269.
$C_{10}H_{11}O_6N$ 6-Nitro-3-methoxy-2-ethoxybenzoic acid (RUBENSTEIN), 2269.
$C_{10}H_{12}O_2N_2$ Malonmonomethylmonophenylamide (WEST), 750.
$C_{10}H_{12}O_3N_2$ Acetonitrobenzylmethylamides (HOLMES and INGOLD), 1818.
$C_{10}H_{12}O_5N_2$ 4-Nitro-2:5-dimethoxyacetanilide (RUBENSTEIN), 2003.
$C_{10}H_{12}O_5S$ *d*-α-*p*-Toluenesulphonoxypropionic acid, rotatory power and reactions of (KENYON, PHILLIPS, and TURLEY), 412.
$C_{10}H_{13}ON$ Acetomethylbenzylamide (HOLMES and INGOLD), 1818.
$C_{10}H_{13}OCl$ α-Chloro-γ-hydroxy-β-phenyl-β-methylpropane (MILLS and BAINS), 2504.

$C_{10}H_{13}OBr$ α-Bromo-γ-hydroxy-β-phenyl-β-methylpropane (Mills and Bains), 2504.

$C_{10}H_{13}O_2N$ γ-Piperonylpropylamine, and its hydrochloride (Baker and Robinson), 1428.

$C_{10}H_{13}O_2Br$ β-Bromocamphorquinone (Burgess and Lowry), 277.

$C_{10}H_{13}O_3N_3$ δ-3-Carbethoxyphenylsemicarbazide, and its hydrochloride (Wilson and Crawford), 107.

$C_{10}H_{15}O_2Br$ Ethyl 2-bromo-Δ^1-*cyclo*hexeneacetate (Baker), 988.

$C_{10}H_{15}O_5Cl$ Ethyl α-chloroacetylsuccinate (Macbeth and Traill), 1120.

$C_{10}H_{16}O_2Br_2$ Ethyl 1:2-dibromo*cyclo*hexane-1-acetate (Baker), 988.

$C_{10}H_{16}O_2Te$ 4-*sec.*-Amyl*cyclo*telluropentane-3:5-dione (Morgan and Elvins), 2624.

$C_{10}H_{17}ON$ Tagetone oxime (Jones and Smith), 2538.

$C_{10}H_{17}ON_3$ α-Methyl-Δ^1-*cyclo*pentenylacetone semicarbazone (Kon and Linstead), 821.

$C_{10}H_{17}O_3N$ *d*-2:2:4-Trimethyl*cyclo*hexan-3-one-1-carboxylic acid oxime (Gibson and Simonsen), 1298.

$C_{10}H_{17}O_3N_3$ 1-Methyl*cyclo*hexan-3-one-1-acetic acid semicarbazone (Farmer and Ross), 2365.

$C_{10}H_{17}O_4Cl$ Ethyl γ-chloro-α-methylglutarate (Ingold), 394.

$C_{10}H_{17}O_4Br$ Ethyl γ-bromo-α-methylglutarate (Ingold), 393.

$C_{10}H_{17}O_4I$ Ethyl α-iodo-α-methylglutarate (Ingold), 394.

$C_{10}H_{19}ON$ γη-Dimethyl-Δ^α-octen-ε-one oxime (Jones and Smith), 2535.

n- and *iso*-Menthoneoximes (Read and Cook), 2786.

$C_{10}H_{19}O_3N_3$ β-*iso*Valeryl-α-methylpropionic acid semicarbazone (Jones and Smith), 2536.

$C_{10}H_{19}O_8N$ Trimethyl methylglucoside 6-mononitrate (Oldham), 2841.

$C_{10}H_{20}O_6S_2$ Menthanedisulphonic acid, barium salt (Kolker and Lapworth), 314.

$C_{10}H_{21}ON$ γη-Dimethyloctan-ε-one oxime (Jones and Smith), 2535.

$C_{10}H_{21}O_6N$ Tetramethyl galactonamide (Pryde, Hirst, and Humphreys), 353.

10 IV

$C_{10}H_7O_2IS$ Naphthalene-2-sulphonyl iodide (Gibson, Miller, and Smiles), 1823.

$C_{10}H_9O_5BrS$ 4-Bromo-2-carboxy-5-methoxyphenylthiolacetic acid (Griffith and Hope), 994.

$C_{10}H_9O_6N_4As$ Glyoxalinecarboxy-*p*-amino-3-nitrophenylarsinic acid, $(+H_2O)$ and its salts (Balaban and King), 2708.

$C_{10}H_{10}O_2N_2Br_2$ Bromomalonmonomethylmono-*p*-bromophenylamide (West), 751.

$C_{10}H_{10}O_4NBr$ 5-Bromo-2-acetylamino-4-methoxybenzoic acid (Griffith and Hope), 993.

$C_{10}H_{10}O_4N_3As$ Glyoxalinecarboxy-*p*-aminophenylarsinic acid, $(+H_2O)$ and its salts (Balaban and King), 2708.

$C_{10}H_{11}OCl_3Te$ Tellurium phenyl-*n*-propylketone trichloride (Morgan and Elvins), 2631.

$C_{10}H_{11}O_2N_2Br$ Bromomalonmono-*p*-tolylamide (West), 752.

$C_{10}H_{11}O_4N_4As$ Glyoxalinecarboxy-*p*-amino-3-aminophenylarsinic acid, $(+\frac{1}{2}H_2O)$ and its salts (Balaban and King), 2709.

$C_{10}H_{12}O_2NCl$ 5-Chloro-2-acetylamino-4-methoxytoluene (Heilbron, Kitchen, Parkes, and Sutton), 2175.

$C_{10}H_{12}O_2NBr$ 5-Bromo-2-acetylamino-*p*-tolyl methyl ether (Griffith and Hope), 992.

$C_{10}H_{12}O_3NBr$ 4-Bromo-2:5-dimethoxyacetanilide (Rubenstein), 2003.

$C_{10}H_{12}O_6NAs$ 3-Acetylamino-4-acetoxyphenylarsinic acid (King and Murch), 2651.
$C_{10}H_{13}ONS$ *iso*Propyl phenylthiocarbamate (Birch and Norris), 904.
$C_{10}H_{13}O_2NS$ *iso*Propyl mercaptan *p*-nitrobenzyl ether (Birch and Norris), 904.
$C_{10}H_{13}O_2SAs$ *p*-Carboxyphenylmethylethylarsine sulphides, and their salts (Mills and Raper), 2481.
$C_{10}H_{13}O_4NS$ *d*-α-*p*-Toluenesulphonoxypropionamide (Kenyon, Phillips, and Turley), 412.
$C_{10}H_{15}O_4SBr$ β-Bromocamphor-α-sulphonic acid, and its salts (Burgess and Lowry), 271.
$C_{10}H_{16}O_2Cl_2Te$ 4-*sec.*-Amyl*cyclo*telluripentane-3:5-dione dichloride (Morgan and Elvins), 2624.
$C_{10}H_{18}O_2Cl_2Te$ Tellurium bismethylpropylketone dichlorides (Morgan and Elvins), 2628.

10 V

$C_{10}H_{12}O_2ClBrS$ α-Bromocamphor-π-chlorosulphoxide (Burgess and Lowry), 282.
$C_{10}H_{14}O_3ClBrS$ β-Bromocamphor-α-sulphonyl chloride (Burgess and Lowry), 271.
$C_{10}H_{15}O_3NBr_2S$ α′β-Dibromocamphor-α-sulphonamide (Burgess and Lowry), 277.
$C_{10}H_{16}O_3NBrS$ β-Bromocamphor-α-sulphonamide (Burgess and Lowry), 275.
$C_{10}H_{18}O_4NBrS$ Acetyl-β-bromocamphor-α-sulphonamide (Burgess and Lowry), 276.

C_{11} Group.

$C_{11}H_8O_5$ Piperonylsuccinic anhydride (Baker and Lapworth), 566.
$C_{11}H_{10}O_4$ 7-Acetoxy-3:4-dihydrocoumarin (Chapman and Stephen), 890.
Anisylsuccinic anhydride (Baker and Lapworth), 566.
$C_{11}H_{10}O_5$ 3-Methoxy-5:7-dihydroxy-2-methylchromone (Kalff and Robinson), 1972.
$C_{11}H_{12}O_2$ 2-Hydroxystyryl ethyl ketone (McGookin and Sinclair), 2542.
$C_{11}H_{12}O_5$ Anisylsuccinic acid (Baker and Lapworth), 565.
$C_{11}H_{12}O_6$ Vanillylsuccinic acid (Baker and Lapworth), 564.
$C_{11}H_{14}O_6$ Δ^1-*cyclo*Hexene-1-acetic-2-malonic acid (Baker), 988.
$C_{11}H_{16}O_2$ β-Phenyl-γ-methylbutylene βγ-glycol, synthesis of (Roger), 522.
$C_{11}H_{16}O_4$ 2:3-Dimethoxybenzaldehyde dimethylacetal (Haworth and Perkin), 1437.
Acetyl derivative of lactone $C_9H_{14}O_3$ (Goodson and Henry), 1648.
$C_{11}H_{18}O_2$ Methyl *l*-2:2:4-trimethyl-Δ^3-*cyclo*hexene-1-carboxylate (Gibson and Simonsen), 1302.
$C_{11}H_{18}O_3$ Ethyl 1-methyl*cyclo*hexan-3-one-1-acetate (Farmer and Ross), 2365.
$C_{11}H_{18}O_3$ Methyl *d*-2:2:4-trimethyl*cyclo*hexan-3-one-1-carboxylate (Gibson and Simonsen), 1299.
$C_{11}H_{18}O_5$ Ethyl α-keto-ββ-dimethylglutarate (Rothstein, Stevenson, and Thorpe), 1079.
$C_{11}H_{18}O_6$ αα′-Dihydroxy*cyclo*heptane-1:1-diacetic acid, and its silver salt (Baker), 1681.
$C_{11}H_{18}N_2$ *cyclo*Hexylidene*cyclo*pentylideneazine (Perkin and Plant), 1141.
$C_{11}H_{20}O_2$ *n*-Octoylacetone, and its copper salt (Morgan and Holmes), 2892.
$C_{11}H_{20}O_3$ Methyl *trans-d*-3-hydroxy-2:2:4-trimethyl*cyclo*hexane-1-carboxylate (Gibson and Simonsen), 1302.
Ethyl *iso*valeryl-α-methylpropionate (Jones and Smith), 2536.

11 III

$C_{11}H_9O_3N$ α-Carbethoxy-γ-hydroxy-γ-phenyl-Δβ-propenecarboxylamide (R. M. and J. N. RÂY), 2722.

$C_{11}H_{10}O_4Br_2$ αα′-Dibromo-β-phenylglutaric acid (HAERDI and THORPE), 1242.

$C_{11}H_{11}ON$ 4-Methoxy-6-methylquinoline (CLEMO and PERKIN), 2305.

$C_{11}H_{11}O_2N_3$ 3-*iso*Propylideneaminotetrahydroquinazoline-2:4-dione (WILSON and CRAWFORD), 109.

$C_{11}H_{11}O_4N$ 2-Carboxy-4:5-dimethoxyphenylacetonitrile (HAWORTH and PINK), 1370.
4:5-Dimethoxyhomophthalimide (HAWORTH and PINK), 1370.

$C_{11}H_{11}O_4Br$ *o*-Bromobenzylidene diacetate (BRADY, COSSON, and ROPER), 2429.

$C_{11}H_{11}N_4Br$ 2-*p*-Bromobenzeneazo-4:5-dimethylglyoxaline, and its hydrochloride (BURTLES and PYMAN), 2014.

$C_{11}H_{12}O_2N_2$ Methoxydimethyl-4-quinazolones (HEILBRON, KITCHEN, PARKES, and SUTTON), 2173.

$C_{11}H_{12}O_5N_2$ Succin-2-nitro-*p*-toluidic acid (BRADY, QUICK, and WELLING), 2267.

$C_{11}H_{12}O_7N_2$ Acetyl derivative of trimethylene glycol monodinitrophenyl ether (FAIRBOURNE and FOSTER), 2762.

$C_{11}H_{12}N_2S$ 2-Ethylthiol-1-phenylglyoxaline, picrate of (BURTLES, PYMAN, and ROYLANCE), 590.

$C_{11}H_{13}ON_3$ *p*-Toluneazoallylformaldoxime (WALKER), 1862.

$C_{11}H_{13}O_2N$ Diacetylbenzylamine (HOLMES and INGOLD), 1820.
6-Ethoxy-4-keto-1:2:3:4-tetrahydroquinoline (CLEMO and PERKIN), 2306.
β-Veratrylpropionitrile (BAKER and ROBINSON), 1433.

$C_{11}H_{13}O_3N$ Acetyl-4-methoxy-3-methyl-α-benzaldoxime (BRADY, COSSON, and ROPER), 2431.

$C_{11}H_{13}O_4N$ Carbethoxymethylanthranilic acid (HEILBRON, KITCHEN, PARKES, and SUTTON), 2171.
5-Nitro-4-allylveratrole (LIONS, PERKIN, and ROBINSON), 1167.

$C_{11}H_{13}O_5N$ 4:5-Dimethoxyhomophthalamic acid (HAWORTH and PINK), 1370.
Nitro-2:3-diethoxybenzaldehydes (RUBENSTEIN), 2269.

$C_{11}H_{13}O_6N$ Methyl 2-cyano*cyclo*butane-1:2:3-tricarboxylate (ING and PERKIN), 2396.

$C_{11}H_{15}O_2N$ 6:7-Dimethoxy-1:2:3:4-tetrahydro*iso*quinoline, and its hydrochloride (FORSYTH, KELLY, and PYMAN), 1666.

$C_{11}H_{14}O_2N_2$ Malonmonoethylmonophenylamide (WEST), 750.
Malonmonomethylmono-*p*-tolylamide (WEST), 751.

$C_{11}H_{15}O_{10}N$ Acetonitropentose (OLDHAM), 2845.

$C_{11}H_{16}O_2N_2$ *neo*Pilocarpines, and their salts (BURTLES, PYMAN, and ROYLANCE), 584.

$C_{11}H_{17}ON_3$ Base, and its salts, from chenopodium oil (HENRY and PAGET), 1656.

$C_{11}H_{17}O_4N$ Ethyl *as*-dimethylcyanosuccinate, preparation and stability of (INGOLD), 472.

$C_{11}H_{18}O_2Te$ 2-*n*-Hexyl*cyclo*telluropentane-3:5-dione (MORGAN and TAYLOR), 805.

$C_{11}H_{19}ON_3$ α-Ethyl-Δ¹-*cyclo*pentenylacetone semicarbazone (KON and LINSTEAD), 821.

$C_{11}H_{19}O_3N$ Methyl *d*-2:2:4-trimethyl*cyclo*hexan-3-one-1-carboxylate oxime (GIBSON and SIMONSEN), 1299.

$C_{11}H_{21}ON_3$ γη-Dimethyl-Δα-octen-ε-one semicarbazone (JONES and SMITH), 2535.
dl-Menthonesemicarbazones (READ and COOK), 2787.

$C_{11}H_{23}ON_3$ γη-Dimethyloctan-ε-one semicarbazone (JONES and SMITH), 2535.
δ-Menthylsemicarbazide, and its hydrochloride (WILSON and CRAWFORD), 106.

11 IV

$C_{11}H_9ONS$ α-Thiocyanostyryl methyl ketone (Challenger and Bott), 1040.

$C_{11}H_{10}O_3NI_3$ Thyroxin, relation of, to tryptophan (Hicks), 771.

$C_{11}H_{12}O_2N_2Br_2$ Bromomalonmonoethylmono-*p*-bromophenylamide (West), 751.

$C_{11}H_{13}ONS$ Substance, from carvone and thiocyanogen (Challenger and Bott), 1041.

$C_{11}H_{13}O_2N_2Br$ Bromomalonmonomethylmono-*p*-tolylamide (West), 751.

$C_{11}H_{14}ON_2S$ 2-Anilino-5-ethoxy-4:5-dihydrothiazole (Burtles, Pyman, and Roylance), 590.

$C_{11}H_{15}ONS$ *iso*Butyl phenylthiocarbamate (Birch and Norris), 905.

$C_{11}H_{18}O_2Cl_2Te$ 2-*n*-Hexyl*cyclo*telluripentane-3:5-dione 1:1-dichloride (Morgan and Taylor), 804.

$C_{11}H_{20}O_2NBr$ 4-Carboxybispiperidinium-1:1′-spiran bromide, and its picrate (Mills and Bains), 2506.

11 V

$C_{11}H_9ONBr_2S$ α-Thiocyanostyryl methyl ketone dibromide (Challenger and Bott), 1041.

C_{12} Group.

$C_{12}H_{10}O_6$ Carboxyphenylparaconic acid (Haerdi and Thorpe), 1246.

$C_{12}H_{10}N_2$ 3-Methyl-3-*iso*carboline (Armit and Robinson), 1612.

$C_{12}H_{14}O_2$ 3-Benzylacetylacetone, and its salts (Morgan and Taylor), 801.

2-Hydroxystyryl *n*-propyl ketone (McGookin and Sinclair), 2542.

β-Phenylpropionylacetone, copper salt (Morgan and Jones), 2619.

$C_{12}H_{14}O_3$ 3-Methoxy-4-hydroxystyryl ethyl ketone (McGookin and Sinclair), 2543.

$C_{12}H_{14}N_2$ 1-Anilino-1-cyano*cyclo*pentane (Plant and Facer), 2038.

$C_{12}H_{16}O_4$ Benzoyl dimethyl glycerol (Gilchrist and Purves), 2743.

Ethyl ethane-$^{1:2}$II$^{1:4}$-1-methyl*cyclo*hexa-3:5-dione-2-carboxylate (Farmer and Ross), 2366.

$C_{12}H_{16}O_5$ ω:3:4:5-Tetramethoxyacetophenone (Pratt and Robinson), 173.

$C_{12}H_{16}O_8$ Dextrin triacetate (Irvine and Oldham), 2915.

Methyl *cyclo*butane-1:2:2:3-tetracarboxylate (Ing and Perkin), 2395.

$C_{12}H_{18}O_5$ Ethyl hydrogen 1-methyl*cyclo*hexan-3-one-4-carboxylate-3-acetate (Farmer and Ross), 2366.

*cyclo*Heptane*spiro*-1-methoxy*cyclo*propane-1:2-dicarboxylic acid (Baker), 1680.

$C_{12}H_{20}O_5$ Ethyl methoxycaronate (Rothstein, Stevenson, and Thorpe), 1079.

$C_{12}H_{20}O_6$ Tetramethylglucose, mutarotation of, in various solvents (Lowry and Richards), 1385.

$C_{12}H_{20}N_2$ *cyclo*Hexylideneazine, action of hydrochloric acid on (Perkin and Plant), 1138.

$C_{12}H_{21}O_4$ 3-*sec.*-Amyldipropionylmethane (Morgan and Elvins), 2624.

$C_{12}H_{22}O_2$ *n*-Nonoylacetone, and its copper salt (Morgan and Holmes), 2893.

$C_{12}H_{22}O_3$ *l*-Menthyl glycollate (Rule and Smith), 2191.

$C_{12}H_{22}O_5$ Diethyl α-keto-ββ-dimethylpentane-αγ-dicarboxylate (Rothstein, Stevenson, and Thorpe), 1077.

Ethyl ester of acid, $C_8H_{14}O_5$ (Goss and Ingold), 2779.

$C_{12}H_{22}O_6$ Ethyl phenyl*cyclo*propanetricarboxylate (Haerdi and Thorpe), 1246.

$C_{12}H_{24}O_2$ Lauric acid, potassium salt, effect of potassium chloride on solutions of (Quick), 1401.

12 III

$C_{12}H_8ClAs$ *oo′*-Diphenylylenearsenious chloride (Aeschlimann, Lees, McCleland, and Nicklin), 68.

$C_{12}H_8Cl_3As$ Di-*p*-chlorophenylchloroarsine (Hunt and Turner), 2671.
$C_{12}H_9O_2As$ *oo'*-Diphenylylenearsinic acid (Aeschlimann, Lees, McCleland, and Nicklin), 68.
$C_{12}H_9O_3As$ Diphenylyl-*o*-arsinic acid (Aeschlimann, Lees, McCleland, and Nicklin), 68.
$C_{12}H_{10}O_2Se$ α-Naphthylselenoglycollic acid (Morgan and Porritt), 1758.
$C_{12}H_{10}N_2S_3$ 4:4'-Diaminodiphenyl trisulphide, and its hydrochloride (Hodgson and Wilson), 443.
$C_{12}H_{11}O_4N$ α-Cyano-β-veratrylacrylic acid (Baker and Robinson), 1432.
$C_{12}H_{11}O_4Br$ Methyl hydrogen 1-bromo-3-phenyl*cyclo*propane-1:2-dicarboxylate (Haerdi and Thorpe), 1244.
$C_{12}H_{11}O_4As$ *o*-Phenoxyphenylarsinic acid (Turner and Sheppard), 546.
$C_{12}H_{11}O_5N_3$ Pyridine 3:5-dinitro-*o*-tolyl oxide (Gibson), 45.
$C_{12}H_{12}O_2N_2$ Ethyl 4(5)-phenylglyoxaline-5(4)-carboxylate (Forsyth and Pyman), 580.
Methyl 3-amino-2-methylcinchoninate (Gulland and Robinson), 1497.
$C_{12}H_{12}O_2Te$ 2-Benzyl*cyclo*telluropentane-3:5-dione (Morgan and Jones), 2620.
4-Benzyl*cyclo*telluropentane-3:5-dione (Morgan and Taylor), 801.
$C_{12}H_{12}O_3N_2$ 6:7-Dimethoxy*iso*quinoline-1-carboxylamide (Haworth and Perkin), 1442.
$C_{12}H_{13}ON$ ψ-Indoxyl*spirocyclo*pentane, alkali salts of (Sidgwick and Plant), 209.
$C_{12}H_{13}O_3N$ Carbethoxy-α-cinnamaldoxime (Brady and McHugh), 2426.
$C_{12}H_{13}O_4N$ α-Cyano-β-veratrylpropionic acid (Baker and Robinson), 1433.
$C_{12}H_{14}O_3N_2$ 1-Anilino*cyclo*pentane-1-carboxynitrosoamine (Plant and Facer), 2039.
$C_{12}H_{15}O_2N$ 1-Anilino*cyclo*pentane-1-carboxylic acid (Plant and Facer), 2039.
$C_{12}H_{15}O_2N_3$ Nitrosoamine of 1-anilino*cyclo*pentane-1-carboxylamide (Plant and Facer), 2039.
$C_{12}H_{15}O_2Br$ α-Bromo-γ-acetoxy-β-phenyl-β-methylpropane (Mills and Bains), 2505.
$C_{12}H_{15}O_3N$ Acetylpiperonylpropylamine (Baker and Robinson), 1429.
$C_{12}H_{16}ON_2$ 1-Anilino*cyclo*pentane-1-carboxylamide (Plant and Facer), 2039.
$C_{12}H_{16}O_2N_2$ Malonmonoethylmono-*p*-tolylamide (West), 751.
$C_{12}H_{17}O_2Br$ Bromoacetoxydihydro-*p*-cymene (Henry and Paget), 1658.
$C_{12}H_{18}O_2N_2$ Ethylenediaminobisacetylacetone, diaquocobalt salt (Morgan and Smith), 2034.
$C_{12}H_{18}O_3N_2$ Diphenylcarbamyl-ɔ-methoxy-β-benzaldoxime (Brady and McHugh), 2426.
$C_{12}H_{20}O_2Te$ 2-*n*-Heptyl*cyclo*telluropentane-3:5-dione (Morgan and Taylor), 805.
$C_{12}H_{21}O_3N_3$ Ethyl 1-methyl*cyclo*hexan-3-one-1-acetate semicarbazone (Farmer and Ross), 2365.
Methyl *d*-2:2:4-trimethyl*cyclo*hexan-3-one-1-carboxylate semicarbazones (Gibson and Simonsen), 1300.
$C_{12}H_{22}O_2N$ *N*-Methylol-Δω-undecenoamide (Jones and Pyman), 2598.

12 IV

$C_{12}H_7OCl_2As$ Dichlorophenoxarsines (Roberts and Turner), 2010.
$C_{12}H_8OClAs$ 6-Chlorophenoxarsine (Turner and Sheppard), 544.
$C_{12}H_8OCl_3As$ Chlorophenoxyphenyldichloroarsines (Roberts and Turner), 2009.
$C_{12}H_8O_3NCl$ Chloronitrodiphenyl ethers (Roberts and Turner), 2008.
$C_{12}H_8O_3ClAs$ Chlorophenoxarsinic acids (Roberts and Turner), 2010.
$C_{12}H_{10}ONCl$ Chloroaminodiphenyl ethers, and their hydrochlorides (Roberts and Turner), 2008.

$C_{12}H_{10}O_4ClAs$ Chlorophenoxyphenylarsinic acids (Roberts and Turner), 2009.
$C_{12}H_{12}O_2N_2S$ Ethyl 2-thiol-4(5)-phenylglyoxaline-5(4)-carboxylate (Forsyth and Pyman), 579.
$C_{12}H_{12}O_2Cl_2Te$ 4-Benzyl*cyclo*telluripentane-3:5-dione 1:1-dichloride (Morgan and Taylor), 801.
$C_{12}H_{14}O_2NI$ 6:7-Dimethoxy*iso*quinoline methiodide (Forsyth, Kelly, and Pyman), 1666.
$C_{12}H_{14}O_2N_2Te$ 4-Benzyl*cyclo*telluropentane-3:5-dionedioxime (Morgan and Taylor), 801.
$C_{12}H_{15}O_2N_2Br$ Bromomalonmonoethylmono-*p*-tolylamide (West), 751.
$C_{12}H_{16}ON_2S$ 2-Anilino-5-ethoxy-4-methyl-4:5-dihydrothiazole, picrate of (Burtles, Pyman, and Royalance), 589.
$C_{12}H_{20}O_2Cl_2Te$ 2-*n*-Heptyl*cyclo*telluripentane-3:5-dione 1:1-dichloride (Morgan and Taylor), 805.
$C_{12}H_{21}O_2Cl_3Te$ Tellurium *n*-nonylacetone trichloride (Morgan and Taylor), 806.
$C_{12}H_{22}O_2Cl_2Te$ Tellurium bismethylbutylketone dichlorides (Morgan and Elvins), 2629.
Tellurium bispinacolin dichloride (Morgan and Elvins), 2630.
$C_{12}H_{29}O_5N_4Co$ Diamminoethylene diaminobisacetonecobaltic hydroxide, salts of (Morgan and Smith), 2034.
$C_{12}H_{36}Cl_2Sb_4Pd$ Tetrakistrimethylstibinepalladous chloride (Morgan and Yarsley), 190.

12 V

$C_{12}H_6O_2Cl_2Br_2S_2$ 2:5-Dibromophenyl 2:5-dichlorobenzenethiolsulphonate (Miller and Smiles), 230.
2:5-Dichlorophenyl 2:5-dibromobenzenethiolsulphonate (Miller and Smiles), 230.
$C_{12}H_7O_4NCl_2S_2$ 2:5-Dichlorophenyl 2-nitrobenzenethiolsulphonate (Miller and Smiles), 230.
2-Nitrophenyl 2:5-dichlorobenzenethiolsulphonate (Miller and Smiles), 229.
$C_{12}H_8O_4NClS_2$ 2-Nitrophenyl 4-chlorobenzenethiolsulphonate (Miller and Smiles), 229.
$C_{12}H_{36}Cl_4SbPtPd$ Tetrakistrimethylstibineplatinous palladochloride (Morgan and Yarsley), 189.

C_{13} Group.

$C_{13}H_{11}As$ Diphenylylenemethylarsine (Aeschlimann, Lees, McCleland, and Nicklin), 69.
$C_{13}H_{12}O_6$ Acetovanillylsuccinic anhydride (Baker and Lapworth), 565.
α-Carbethoxy-γ-hydroxy-γ-phenyl-Δβ-propenecarboxylactone (R. M. and J. N. Rây), 2722.
Ethyl 4-hydroxymethyl-1:2-phthalideoxalate (Perkin and Stone), 2287.
$C_{13}H_{12}O_7$ 2:4:6-Triacetoxybenzaldehyde ($+\frac{1}{2}H_2O$) (Pratt and Robinson), 1184.
$C_{13}H_{13}N$ Benzylaniline, reactions of antimony halides with (Vanstone), 552.
$C_{13}H_{14}O_5$ 2-Ethoxy-3-phenyl*cyclo*propane-1:2-dicarboxylic acid, and its silver salt (Haerdi and Thorpe), 1242.
$C_{13}H_{16}O_2$ 3-Benzylpropionylacetone, and its copper salt (Morgan and Corby), 2618.
$C_{13}H_{16}O_3$ 3-Methoxy-4-hydroxystyryl *n*-propyl ketone (McGookin and Sinclair), 2543.
$C_{13}H_{20}O_2$ β-Phenyl-γ-ethylamylene βγ-glycol (Roger), 523.
$C_{13}H_{20}O_6$ γδ-Dicarbethoxy-γ-hydroxy-ββ-dimethylbutane-α-carboxylactone (Rothstein, Stevenson, and Thorpe), 1080.

$C_{13}H_{20}O_9$ Triacetyl methylglucoside (Oldham), 2844.
$C_{13}H_{22}O_4$ *l*-Menthyl hydrogen malonate (Rule and Smith), 2192.
$C_{13}H_{22}O_6$ Ethyl *as*-dimethylcarboxysuccinate (Ingold), 473.
$C_{13}H_{24}O_3$ *l*-Menthyl methoxyacetate (Rule and Smith), 2191.
$C_{13}H_{24}O_6$ Ethyl $\beta\beta'$-dimethoxydiethylmalonate (Bennett), 1279.

13 III

$C_{13}H_7O_9N_5$ Picrylnitrobenz*syn*aldoximes (Brady and Klein), 846.
$C_{13}H_8O_7N_4$ Picrylbenz*syn*aldoxime (Brady and Klein), 846.
$C_{13}H_8N_2Cl_4$ Benzaldehydetetrachlorophenylhydrazone (Humphries, Humble, and Evans), 1307.
$C_{13}H_8NAs$ *oo'*-Diphenylylenearsenious cyanide (Aeschlimann, Lees, McCleland, and Nicklin), 69.
$C_{13}H_9N_2Cl_3$ Benzaldehyde-*p*-chlorophenylhydrazone (Humphries, Humble, and Evans), 1306.
Chlorobenzaldehyde-2:4-dichlorophenylhydrazones (Humphries, Humble, and Evans), 1307.
$C_{13}H_9N_2Br_3$ Bromobenzaldehyde-2:4-dibromophenylhydrazones (Chattaway and Walker), 980.
$C_{13}H_{10}O_2N_2$ Anhydro-3-acetylamino-2-methylcinchoninic acid (Gulland and Robinson), 1498.
$C_{13}H_{10}O_4N_2$ *m*-Nitrophenyl phenylcarbamate (Brady and Harris), 2175.
$C_{13}H_{10}O_5N_4$ Nitrohydroxybenzaldehyde-*p*-nitrophenylhydrazones (Hodgson and Beard), 880.
$C_{13}H_{11}ON$ Benzanilide, reactions of antimony halides with (Vanstone), 550.
$C_{13}H_{11}O_2N$ Phenyl*cyclo*iminotoluquinone (Chattaway and Parkes), 1310.
$C_{13}H_{11}O_2N_3$ Phenylaziminotoluquinone (Chattaway and Parkes), 1309.
$C_{13}H_{11}N_3Br_2$ Benzaldehyde-2:4-dibromophenylhydrazidine (Chattaway and Walker), 981.
$C_{13}H_{12}O_3N_2$ 3-Acetylamino-2-methylcinchoninic acid (Gulland and Robinson), 1497.
$C_{13}H_{12}BrAs$ *p*-Bromodiphenylmethylarsine (Hunt and Turner), 2670.
$C_{13}H_{13}ON_3$ 3-*p*-Hydroxybenzeneazo-2:6-lutidine, and its hydrochloride (Gulland and Robinson), 1495.
$C_{13}H_{13}O_4Br$ Methyl 1-bromo-3-phenyl*cyclo*propane-1:2-dicarboxylate (Haerdi and Thorpe), 1244.
Lactone of ethyl α-bromo-α'-hydroxy-β-phenylglutarate (Haerdi and Thorpe), 1241.
$C_{13}H_{14}ON_4$ 2:4:2':4'-Tetra-aminobenzophenone (Gulland and Robinson), 1499.
$C_{13}H_{14}O_2Te$ 4-Benzyl-2-methyl*cyclo*telluropentane-3:5-dione (Morgan and Corby), 2618.
$C_{13}H_{14}O_8N_2$ *iso*Propylidene glycerol 3:5-dinitrobenzoate (Fairbourne and Foster), 2763.
$C_{13}H_{14}O_4Br_2$ Methyl $\alpha\alpha'$-dibromo-β-phenylglutarate (Haerdi and Thorpe), 1241.
$C_{13}H_{15}O_2N$ Dimethoxy-2:4-dimethylquinolines, and their salts (Lions, Perkin, and Robinson), 1162.
$C_{21}H_{15}O_2N_3$ 3-Diphenylmethyleneaminotetrahydroquinazoline-2:4-dione (Wilson and Crawford), 108.
$C_{13}H_{15}O_4N$ δ-*o*-Formylaminobenzoylvaleric acid (Paterson and Plant), 1798.
$C_{13}H_{15}O_4Br$ Methyl α-bromo-β-phenylglutarate (Haerdi and Thorpe), 1241.
$C_{13}H_{17}ON$ Methylpentenoic acid *p*-toluidides (Kon and Linstead), 623.
$C_{13}H_{17}O_3N$ 5-Acetylamino-4-allylveratrole (Lions, Perkin, and Robinson), 1168.
β Dimethoxyanilinopropenyl methyl ketones (Lions, Perkin, and Robinson), 1162.

$C_{13}H_{17}O_3N_3$ Acetone-δ-carbethoxyphenylsemicarbazones (Wilson and Crawford), 108.

$C_{13}H_{18}O_2N_2$ Malonmono*iso*propylmono-*p*-tolylamide (West), 751.

$C_{13}H_{18}O_3N_2$ Anhydrocotarninemethylamine, and its salts (Haworth and Perkin), 1444.

$C_{13}H_{19}O_2N$ Dimethoxy-2:4-dimethyl-1:2:3:4-tetrahydroquinolines, and their salts (Lions, Perkin, and Robinson), 1162.

$C_{13}H_{19}O_8I$ Triacetyl methylglucoside 6-iodohydrin (Oldham), 2844.

$C_{13}H_{19}O_{11}N$ Triacetyl methylglucoside 6-nitrate (Oldham), 2843.

13 IV

$C_{13}H_6O_2N_3Cl_3$ 1-Trichlorophenyl-3-*o*-nitrophenyl*iso*diazomethanes (Chattaway and Walker), 2412.

$C_{13}H_7O_2N_3Cl_2$ 1-2:4-Dichlorophenyl-3-*o*-nitrophenyl*iso*diazomethane (Chattaway and Walker), 2412.

$C_{13}H_7O_2N_3Cl_4$ ω-Chloronitrobenzaldehydetrichlorophenylhydrazones (Chattaway and Walker), 1690, 2413.

$C_{13}H_7O_2N_3Br_2$ 1-2:4-Dibromophenyl-3-*o*-nitrophenyl*iso*diazomethane (Chattaway and Walker), 2411.

$C_{13}H_7O_2N_3Br_4$ ω-Bromo-*m*-nitrobenzaldehydetribromophenylhydrazone (Chattaway and Walker), 1695.

$C_{13}H_8O_2NBr_3$ 2:4:6-Tribromophenyl*cyclo*iminotoluquinone (Chattaway and Parkes), 1311.

$C_{13}H_8O_2N_3Cl$ 1-*p*-Chlorophenyl-3-*o*-nitrophenyl*iso*diazomethane (Chattaway and Walker), 2412.

$C_{13}H_8O_2N_3Cl_3$ ω-Chloronitrobenzaldehydedichlorophenylhydrazones (Chattaway and Walker), 1691, 2413.

$C_{13}H_8O_2N_3Br$ 1-*p*-Bromophenyl-3-*o*-nitrophenyl*iso*diazomethane (Chattaway and Walker), 2410.

$C_{13}H_8O_2N_3Br_3$ ω-Bromonitrobenzaldehydedibromophenylhydrazones (Chattaway and Walker), 1695, 2411.

$C_{13}H_8O_3NBr_3$ *s*-Tribromophenyl *p*-nitrobenzyl ether (Holmes and Ingold), 1809.

$C_{13}H_8O_3N_3Cl_3$ β-Nitrobenzoyltrichlorophenylhydrazines (Chattaway and Walker), 1698.

$C_{13}H_8O_4NCl$ 3-Chloro-2-nitrophenyl benzoate (Hodgson and Moore), 1601.

$C_{13}H_9O_2NCl_2$ Dichlorophenyl*cyclo*iminotoluquinones (Chattaway and Parkes), 1311.

$C_{13}H_9O_2NBr_2$ 2:4-Dibromophenyl*cyclo*iminotoluquinone (Chattaway and Parkes), 1311.

$C_{13}H_9O_3N_3Cl_2$ ω-Chloronitrobenzaldehydechlorophenylhydrazones (Chattaway and Walker), 1690.

$C_{13}H_9O_3N_3Br_2$ ω-Bromonitrobenzaldehydebromophenylhydrazones (Chattaway and Walker), 1695.

$C_{13}H_9O_2N_4Cl_3$ Nitrobenzaldehydetrichlorophenylhydrazidines (Chattaway and Walker), 1694.

$C_{13}H_9O_3N_3Br_2$ 4:6-Dibromo-3-hydroxybenzaldehyde-*p*-nitrophenylhydrazone (Hodgson and Beard), 881.

β-Nitrobenzoyldibromophenylhydrazines (Chattaway and Walker), 1698.

$C_{13}H_9N_2ClBr_2$ ω-Chlorobenzaldehyde-2:4-dibromophenylhydrazone (Chattaway and Walker), 981.

$C_{13}H_{10}O_2NCl$ *p*-Chlorophenyl*cyclo*iminotoluquinone (Chattaway and Parkes), 1311.

$C_{13}H_{10}O_2NBr$ *p*-Bromophenyl*cyclo*iminotoluquinone (Chattaway and Parkes), 1311.

$C_{13}H_{10}O_2N_4Cl_2$ *m*-Nitrobenzaldehyde-2:4-dichlorophenylhydrazidine, and its hydrochloride (CHATTAWAY and WALKER), 1694.

$C_{13}H_{10}O_2N_4Br_2$ Nitrobenzaldehydedibromophenylhydrazidines, and their hydrochlorides (CHATTAWAY and WALKER), 1697.

$C_{13}H_{10}O_2Cl_2S_2$ 4-Tolyl 2:5-dichlorobenzenethiolsulphonate (GIBSON, MILLER, and SMILES), 1824.

$C_{13}H_{10}O_3N_3Br$ Bromohydroxybenzaldehyde-*p*-nitrophenylhydrazones (HODGSON and BEARD), 881.

$C_{13}H_{10}O_8N_3As$ Dinitrobenzoyl-4-aminophenylarsinic acids (KING and MURCH), 2637.

$C_{13}H_{10}N_2Br_3S$ 1-Anilinobenzthiazole tribromide (HUNTER), 2025.

$C_{13}H_{11}O_2NS_2$ Benzyl 2-nitrophenyl disulphide (FOOTNER and SMILES), 2889.

$C_{13}H_{11}O_2N_4Cl$ *m*-Nitrobenzaldehyde-*p*-chlorophenylhydrazidine (CHATTAWAY and WALKER), 1694.

$C_{13}H_{11}O_2N_4Br$ Nitrobenzaldehydebromophenylhydrazidine, and their hydrochlorides (CHATTAWAY and WALKER), 1697.

$C_{13}H_{11}O_4NS_2$ 2-Nitrophenyl 4-toluenethiolsulphonate (MILLER and SMILES), 229.
4-Tolyl 3-nitrobenzenethiolsulphonate (GIBSON, MILLER, and SMILES), 1822.

$C_{13}H_{11}O_7N_2As$ 3′-Nitro-4′-hydroxybenzoyl-4-aminophenylarsinic acid (KING and MURCH), 2649.

$C_{13}H_{13}O_5N_2As$ 3′-Amino-4′-hydroxybenzoyl-4-aminophenylarsinic acid, and its sodium salt (KING and MURCH), 2650.

$C_{13}H_{13}O_6N_2As$ 3′-Nitro-4′-toluoyl-4-aminophenyl (KING and MURCH), 2639.

$C_{13}H_{14}O_2NBr$ 8-Bromo-5:6-dimethoxy-2:4-dimethylquinoline, and its hydrochloride (LIONS, PERKIN, and ROBINSON), 1165.

$C_{13}H_{14}O_2Cl_2Te$ 4-Benzyl-2-methyl*cyclo*telluripentane-3:5-dione 1:1-dichloride (MORGAN and CORBY), 2618.

$C_{13}H_{14}O_4N_3As$ 3:3′-Diaminobenzoyl-4-aminophenylarsinic acid (KING and MURCH), 2638.

$C_{13}H_{16}O_3NBr$ β-6-Bromo-3:4-dimethoxyanilinopropenyl methyl ketone (LIONS, PERKIN, and ROBINSON), 1164.

$C_{13}H_{17}O_2N_2Br$ Bromomalonmono*iso*propylmono-*p*-tolylamide (WEST), 752.

$C_{13}H_{18}ON_2S$ 2-*m*-Xylidino-5-ethoxy-4:5-dihydrothiazole, and its picrate (NIMKAR and PYMAN), 2746.

$C_{13}H_{20}O_2NBr$ Diethylammonium β-bromo-β-phenylpropionate (SENTER and WARD), 1849.

$C_{13}H_{20}O_2NI$ γ-Piperonylpropyltrimethylammonium iodide (BAKER and ROBINSON), 1429.

13 V

$C_{13}H_7O_2N_3Cl_3Br$ ω-Bromo-*o*-nitrobenzaldehydetrichlorophenylhydrazones (CHATTAWAY and WALKER), 2412.

$C_{13}H_8O_2N_3Cl_2Br$ ω-Bromo-*o*-nitrobenzaldehyde-2:4-dichlorophenylhydrazone (CHATTAWAY and WALKER), 2411.

$C_{13}H_9O_2N_3ClBr$ ω-Bromo-*m*-nitrobenzaldehyde-*p*-chlorophenylhydrazone (CHATTAWAY and WALKER), 1695.

$C_{13}H_9O_8N_3ClAs$ 4′-Chloro-3:3′-dinitrobenzoyl-4-aminophenylarsinic acid (KING and MURCH), 2647.

$C_{13}H_{10}O_6N_2ClAs$ 4′-Chloro-3′-nitrobenzoyl-4-aminophenylarsinic acid (KING and MURCH), 2647.

$C_{13}H_{12}O_4N_2ClAs$ 4′-Chloro-3′-aminobenzoyl-4-aminophenylarsinic acid, and its salts (KING and MURCH), 2647.

$C_{13}H_{13}O_4N_3ClAs$ 4′-Chloro-3:3′-diaminobenzoyl-4-aminophenylarsinic acid (KING and MURCH), 2648.

C_{14} Group.

$C_{14}H_5Cl_9$ Nonochlorophenyltolylmethane (Silberrad), 2684.
$C_{14}H_8O_2$ Phenanthraquinone, action of hydrazine hydrate on (Dutt), 2971.
$C_{14}H_{10}O_4$ 2:4-Dihydroxybenzil (Marsh and Stephen), 1636.
$C_{14}H_{10}O_5$ 2:4:6-Trihydroxybenzil (Marsh and Stephen), 1637.
$C_{14}H_{12}O_6$ Acid, from ethyl dibromocinnamate and ethyl sodiomalonate (Haerdi and Thorpe), 1247.
$C_{14}H_{14}O_2$ Methylbenzoin (Roger), 523.
$C_{14}H_{15}As$ Phenyl-*p*-tolylmethylarsine (Hunt and Turner), 2668.
$C_{14}H_{16}O_8$ Carbethoxyvanillylsuccinic acid (Baker and Lapworth), 565.
$C_{14}H_{18}O_4$ β-Phenyl-β-methylpropane αγ-diacetate (Mills and Bains), 2504.
$C_{14}H_{20}O_5$ Ethyl 1-methyl*cyclo*hexan-3-one-4-carboxylate-1-acetate (Farmer and Ross), 2366.
$C_{14}H_{22}O_5$ Ethyl 1-methyl*cyclo*hexan-3-one-4-carboxylate-1-acetate (Farmer and Ross), 2364.
$C_{14}H_{22}O_9$ δε-Dicarbethoxy-δ-hydroxy-γγ-dimethylpentane-β-carboxylactone (Rothstein, Stevenson, and Thorpe), 1078.
$C_{14}H_{26}O_2$ *n*-Undecoylacetone, and its copper salt (Morgan and Holmes), 2893.
$C_{14}H_{26}O_3$ *l*-Menthyl ethoxyacetate (Rule and Smith), 2191.

14 III

$C_{14}H_8O_9N_4$ Picryl-3:4-methylenedioxybenz*syn*aldoxime (Brady and Klein), 846.
$C_{14}H_9N_3Br_2$ ω-Cyanobenzaldehyde-2:4-dibromophenylhydrazone (Chattaway and Walker), 982.
$C_{14}H_{10}O_4N$ Benzoyl-3:4-methylenedioxy-α-benzaldoxime (Brady and McHugh), 2420.
$C_{14}H_{10}O_4N_2$ Benzoylnitro-α-benzaldoximes (Brady and McHugh), 2420.
$C_{14}H_{10}O_5N_2$ 2:4-Dinitro-2′-hydroxystilbene (Gulland and Robinson), 1503.
$C_{14}H_{10}O_6N_2$ 3:5-Dinitro-*o*-tolyl benzoate (Gibson), 47.
$C_{14}H_{10}O_8N_4$ Picrylmethoxybens*syn*aldoximes (Brady and Klein), 846.
$C_{14}H_{11}O_3N$ Phenyl-4-pyridylpyruvic acid (Singh), 2448.
$C_{14}H_{11}O_4N$ Nitro-*o*-tolyl benzoates (Gibson), 46.
$C_{14}H_{11}O_4N_3$ Nitrobenzylidenenitrobenzylamines (Ingold), 1143.
$C_{14}H_{12}O_3N_4$ Phthalaldehyde 1-oxime-2-*p*-nitrophenylhydrazone (Griffiths and Ingold), 1705.
$C_{14}H_{12}O_5N_4$ 4-Nitro-3-methoxybenzaldehyde-*p*-nitrophenylhydrazone (Hodgson and Beard), 881.
$C_{14}H_{12}N_2Cl_2$ Acetophenone-2:4-dichlorophenylhydrazone (Humphries, Humble, and Evans), 1306.
$C_{14}H_{12}N_2S$ 4′-Amino-1-methyl-5-methylbenzthiazole, bromination of (Hunter), 1318.
$C_{14}H_{13}ON_3$ Benzeneazobenzylformaldoxime (Walker), 1860.
$C_{14}H_{13}OAs$ 10-Ethylphenoxarsine (Aeschlimann), 813.
$C_{14}H_{13}O_2N$ *o*-Acetylaminodiphenyl ether (Roberts and Turner), 2008.
o-Tolyl*cyclo*iminotoluquinone (Chattaway and Parkes), 1310.
$C_{14}H_{13}O_2N_3$ Tolualdehyde *p*-nitrophenylhydrazones (Stephen), 1877.
$C_{14}H_{13}O_2As$ *o*-Carboxydiphenylmethylarsine (Aeschlimann), 812.
10-Ethylphenoxarsine oxide ($+H_2O$) (Aeschlimann), 814.
$C_{14}H_{13}O_3As$ *o*-Carboxydiphenylmethylarsine oxide (Aeschlimann), 813.
$C_{14}H_{13}O_4N_3$ Dinitrodibenzylamines, and their salts (Holmes and Ingold), 1815.
$C_{14}H_{14}ON_2$ 2-Hydroxy-3:3′-dimethylazobenzene (Cumming and Ferrier), 2377.
$C_{14}H_{14}O_4S_5$ Phenylmethylsulphone *m*-disulphide (Twist and Smiles), 1251.

$C_{14}H_{14}O_4Te_2$ Bis-2-hydroxy-1-methoxyphenyl 4:4-ditelluride (Morgan and Drew), 2314.

$C_{14}H_{14}O_6S_4$ Phenylmethylsulphone *m*-disulphoxide (Twist and Smiles), 1251.

$C_{14}H_{14}IAs$ Diphenylylenedimethylarsonium iodide (Aeschlimann, Lees, McCleland, and Nicklin), 69.

$C_{14}H_{15}ON_3$ Lutidineazoanisole, and its hydrochloride (Gulland and Robinson), 1496.

$C_{14}H_{15}O_3N$ γ-4-Hydroxy-2-methylquinoline-3-butyric acid (Paterson and Plant), 1798.

$C_{14}H_{15}O_5N_3$ Acetodinitrodibenzylamides (Holmes and Ingold), 1820.

$C_{14}H_{16}O_6S$ Thioindican (Craik and Macbeth), 1639.

$C_{14}H_{17}O_2N$ Substance, from dehydroseretholemethine methiodide and silver oxide (Stedman and Barger), 255.

$C_{14}H_{17}O_4N$ δ-*o*-Acetylaminobenzoylvaleric acid (Paterson and Plant), 1798.

$C_{14}H_{17}O_4N_3$ β-Methylpimelic-β-acetic acid (Farmer and Ross), 2368.

$C_{14}H_{19}ON$ Ethylpentenoic acid *p*-toluidide (Kon and Linstead), 622.

$C_{14}H_{19}O_2N$ Etheserolene, picrate of (Stedman and Barger), 257.

5-Ethoxy-1:3-dimethyl-3-ethyl-2-indoline (Stedman and Barger), 251, 255.

$C_{14}H_{19}O_6N$ Ethyl 2-cyano*cyclo*butane-1:2:3-tricarboxylate (Ing and Perkin), 2396.

$C_{14}H_{19}O_{12}N$ Tetra-acetyl glucose 6-nitrate (Oldham), 2843.

$C_{14}H_{20}O_2N_2$ Malonmono*iso*butylmono-*p*-tolylamide (West), 751.

$C_{14}H_{21}O_2N_3$ *n*-Octaldehyde *p*-nitrophenylhydrazone (Stephen), 1875.

$C_{14}H_{23}O_2N$ β-Anilinobutaldehyde diethylacetal (Mason), 1033.

$C_{14}H_{27}ON_3$ Acetone-δ-menthylsemicarbazone (Wilson and Crawford), 106.

14 IV

$C_{14}H_6O_3NBr_3$ 2:3:9-Tribromo-9-nitroanthrone (Barnett), 2044.

$C_{14}H_8O_4N_2Cl_2$ Dichloro-9:10-dinitro-9:10-dihydroanthracenes (Barnett), 2042.

$C_{14}H_8N_2Br_4S_2$ 1:1-Bisbenzthiazole tetrabromide (Hunter), 1320.

$C_{14}H_9O_4N_2Cl_3$ 1:5:9-Trichloro-9:10-dinitro-9:10-dihydroanthracene (Barnett), 2044.

$C_{14}H_9O_4N_2Br$ 9-Bromo-9:10-dinitro-9:10-dihydroanthracene (Barnett), 2043.

$C_{14}H_9NIS$ 1-Phenylbenzthiazole methiodide (Clark), 974.

$C_{14}H_{11}OCl_3Te$ Tellurium phenylbenzylketone trichloride (Morgan and Elvins), 2631.

$C_{14}H_{12}O_2Cl_2S_2$ 4-Chloroanisole 2-disulphide (Gauntlett and Smiles), 2746.

$C_{14}H_{12}O_3N_3Br$ Bromomethoxybenzaldehyde-*p*-nitrophenylhydrazones (Hodgson and Beard), 881.

$C_{14}H_{12}O_4Cl_2S_2$ 4-Chloroanisole-2-disulphoxide (Gauntlett and Smiles), 2746.

$C_{14}H_{12}O_8N_3As$ 3:3′-Dinitro-4′-toluoyl-4-aminophenylarsinic acid (King and Murch), 2640.

$C_{14}H_{12}O_9N_3As$ Dinitro-4′-anisoyl-4-aminophenylarsinic acids (King and Murch), 2644.

$C_{14}H_{13}O_3N_2Cl$ Phenylpyridylpyruvic acid oxime hydrochloride (Singh), 2448.

$C_{14}H_{13}O_5NS$ Nitro-*o*-tolyl toluene-*p*-sulphonates (Gibson), 47.

$C_{14}H_{13}O_5SAs$ Sulpho-10-ethylphenoxarsine oxide (Aeschlimann), 814.

$C_{14}H_{13}O_7N_2As$ 3′-Nitro-4′-anisoyl-4-aminophenylarsinic acid (King and Murch), 2641.

$C_{14}H_{15}O_2NS$ *p*-Toluenesulphonbenzylamide (Holmes and Ingold), 1812.

$C_{14}H_{15}O_5N_2As$ 3′-Amino-4′-anisoyl-4-aminophenylarsinic acid, and its salts (King and Murch), 2642.

$C_{14}H_{15}BrIAs$ *p*-Bromodiphenyldimethylarsonium iodide (Hunt and Turner), 2670.

$C_{14}H_{16}O_4N_3As$ 3:3′-Diamino-4′-toluoyl-4-aminophenylarsinic acid (King and Murch), 2640.

$C_{14}H_{16}N_2Cl_6Sn$ Benzaldehyde stannichloride (Stephen), 1876.

$C_{14}H_{19}O_2N_2Br$ Bromomalonmono*iso*butylmono-*p*-tolylamide (West), 752.

$C_{14}H_{22}O_2N_2S$ α-Propionacetalylphenylthiocarbamide (Burtles, Pyman, and Roylance), 589.

C_{15} Group.

$C_{15}H_{18}$ Tri*cyclo*trimethylenebenzene (Perkin and Plant), 1140.

$C_{15}H_{24}$ Hydrocarbon, from cedrene and formic acid (Robertson, Kerr, and Henderson), 1946.

Hydrocarbon, from formic acid and cadinene (Robertson, Kerr, and Henderson), 1946.

15 II

$C_{15}H_{10}O_4$ Alizarin 2-methyl ether (Kubota and Perkin), 1893.

$C_{15}H_{10}O_5$ Anthragallol methyl ethers (Kubota and Perkin), 1893.

$C_{15}H_{10}O_6$ Datiscetin, synthesis of (Kalff and Robinson), 1968.

$C_{15}H_{11}N$ α-Acenaphthaquinoline, and its picrate (Stewart), 1331.

$C_{15}H_{12}O_2$ Phenyl benzyl diketone (Malkin and Robinson), 369.

$C_{15}H_{12}O_3$ Hydroxymethoxyanthrones (Miller and Perkin), 2688.

$C_{15}H_{12}O_5$ Dihydroxymethoxybenzils (Marsh and Stephens), 1636.

$C_{15}H_{12}O_6$ Trihydroxymethoxybenzils (Marsh and Stephen), 1637.

$C_{15}H_{13}N$ 1-Methyl-2-methylene-1:2-dihydro-β-naphthaquinoline (Mills and Raper), 2472.

$C_{15}H_{14}O_3$ α-Benzylmandelic acid (Malkin and Robinson), 374.

$C_{15}H_{14}O_4$ Benzylphloracetophenone (Baker), 2355.

$C_{15}H_{14}O_5$ Dihydroxyphenyl β-dihydroxyphenylethyl ketones (Chapman and Stephen), 891.

Ethyl α-acetyl-γ-hydroxy-γ-phenyl-Δ$^{\beta}$-propenecarboxylactone (R. M. and J. N. Rây), 2722.

$C_{15}H_{16}O_4$ Lactone, from ethyl sodioethylmalonate and phenacyl bromide (R. M. and J. N. Rây), 2723.

$C_{15}H_{17}N$ Dibenzylmethylamine, and its hydrochloride (Holmes and Ingold), 1816.

$C_{15}H_{18}O_5$ Methyl 2-ethoxy-3-phenyl*cyclo*propane-1:2-dicarboxylate (Haerdi and Thorpe), 1243.

$C_{15}H_{20}O_2$ 2-Hydroxystyryl *n*-hexyl ketone (McGookin and Sinclair), 2543.

$C_{15}H_{22}O_3$ Ngaione (McDowall), 2202.

$C_{15}H_{22}O_7$ Ethyl 2-acetyl*cyclo*butane-1:2:3-tricarboxylate (Ing and Perkin), 2397.

$C_{15}H_{24}O_3$ Ngaiol (McDowall), 2205.

$C_{15}H_{28}O_2$ Lauroylacetone, and its copper salt (Morgan and Holmes), 2894.

$C_{15}H_{28}O_8$ Diacetalmalonic acid, and its barium salt (Perkin and Pink), 192.

$C_{15}H_{30}O_6$ Hexamethyl glycerol glucoside (Gilchrist and Purves), 2740.

15 III

$C_{15}H_9O_4N$ α-Naphthaquinoline-6:7-dicarboxylic acid (Stewart), 1331.

$C_{15}H_9NS$ 9-Anthryl thiocyanate (Footner and Smiles), 2890.

$C_{15}H_{10}O_3N_2$ Anhydro-2-aldehydoterephthalic acid phenylhydrazone (Perkin and Stone), 2294.

$C_{15}H_{10}O_4N_2$ 3-Nitrophthal-*p*-tolil (Brady, Quick, and Welling), 2267.

$C_{15}H_{10}O_6N_2$ 2:4-Dinitro-3′:4′-methylenedioxystilbene (Gulland and Robinson), 1502.

$C_{15}H_{10}O_7N_4$ Picrylcinnam*syn*aldoxime (Brady and Klein), 847.

$C_{15}H_{11}O_3Cl$ Chrysinidin chloride ($+2H_2O$) (Pratt and Robinson), 1132.
$C_{15}H_{11}O_4Cl$ Apigeninidin chloride ($+2H_2O$) (Pratt and Robinson), 1133.
Galanginidin chloride (Pratt and Robinson), 1135; (Malkin and Robinson), 1193.
$C_{15}H_{11}O_4I$ Galanginidin iodide (Pratt and Robinson), 1135.
$C_{15}H_{11}O_5Cl$ Datiscetinidin chloride ($+H_2O$) (Pratt and Robinson), 1185.
Fisetinidin chloride ($+\frac{1}{2}H_2O$) (Pratt and Robinson), 1136.
Lotoflavinidin chloride ($+2H_2O$) (Pratt and Robinson), 1134.
Luteolinidin chloride ($+2H_2O$) (Pratt and Robinson), 1135.
Pelargonidin chloride ($+H_2O$) (Malkin and Robinson), 1194.
3:5:7:3′-Tetrahydroxyflavylium chloride (Pratt and Robinson), 1186.
$C_{15}H_{11}O_5N_3$ 4-Aldehydo-1:2-hydroxyphthalide *p*-nitrophenylhydrazone (Perkin and Stone), 2293.
$C_{15}H_{11}O_6Cl$ Cyanidin chloride ($+H_2O$) (Pratt and Robinson), 172.
Morinidin chloride ($+2H_2O$) (Pratt and Robinson), 1137.
$C_{15}H_{11}O_7Cl$ Delphinidin chloride (Pratt and Robinson), 174, 1190.
$C_{15}H_{12}O_2N_2$ 4-Aldehydo-1:2-phthalide phenylhydrazone (Perkin and Stone), 2290.
$C_{15}H_{12}O_4N_2$ 4-Aldehydophthalic acid phenylhydrazone (Perkin and Stone), 2295.
Carbanilino-3:4-methylenedioxybenzaldoximes (Brady and McHugh), 2424.
4-Nitro-2-amino-3′:4′-methylenedioxystilbene (Gulland and Robinson), 1502.
$C_{15}H_{12}O_5N_2$ Phthal-2-nitro-*p*-toluidic acid (Brady, Quick, and Welling), 2267.
$C_{15}H_{12}O_6N_2$ 2:4-Dinitro-3′-methoxy-4′-hydroxystilbene (Gulland and Robinson), 1503.
$C_{15}H_{12}O_{10}N_2$ Trimethylene glycol bis-2:4-dinitrophenyl ether (Fairbourne and Foster), 2762.
$C_{15}H_{13}O_2N$ Benzilmonoxime methyl ethers (Brady and Perry), 2876.
$C_{15}H_{13}O_3N$ Anisylidene-*p*-aminobenzoic acid (Wayne and Cohen), 460.
Benzoyl-*o*-methoxy-*α*-benzaldoxime (Brady and McHugh), 2421.
Phthalobenzylamic acid (Holmes and Ingold), 1810.
$C_{15}H_{13}O_7N_5$ Picryl-*p*-dimethylaminobenz*syn*aldoxime (Brady and Klein), 847.
$C_{15}H_{14}O_3N_2$ Carbanilino-*o*-methoxy-*α*-benzaldoxime (Brady and McHugh), 2425.
$C_{15}H_{14}N_2S$ 1-*m*-Toluidino-*m*-toluthiazole (Hunter), 2027.
$C_{15}H_{15}ON_3$ Phenylpyruvic acid oxime (Walker), 1862.
$C_{15}H_{15}O_2N_3$ Benzoinsemicarbazone (Hopper), 1285.
p-Tolylacetaldehyde *p*-nitrophenylhydrazone (Stephen), 1877.
$C_{15}H_{15}O_4N_3$ Dinitrodibenzylmethylamines, and their hydrochlorides (Holmes and Ingold), 1817.
$C_{15}H_{17}ON$ *β*-Amino-*αα*-diphenyl-*n*-propyl alcohol (McKenzie and Wills), 288.
$C_{15}H_{17}O_2N$ Benzylnorhydrohydrastinine, and its salts (Haworth, Perkin, and Pink), 1721.
$C_{15}H_{18}O_4Br_2$ Ethyl *αα*′-dibromo-*β*-phenylglutarate (Haerdi and Thorpe), 1241.
$C_{15}H_{18}IAs$ Phenyl-*p*-tolyldimethylarsonium iodide (Hunt and Turner), 2668.
$C_{15}H_{19}O_7N_5$ Trinitroeserethole (Stedman and Barger), 256.
$C_{15}H_{20}O_2N_2$ Substance, and its salts, from oxidation of eserethole (Stedman and Barger), 256.
$C_{15}H_{20}O_5N_2$ 6-Nitro-1-acetyl-5:8-dimethoxy-2:4-dimethyl-1:2:3:4-tetrahydroquinoline (Lions, Perkin, and Robinson), 1163.
$C_{15}H_{21}O_2N_3$ Eserine (Stedman and Barger), 247.
$C_{15}H_{21}O_2N$ Acetyl derivatives of dimethoxydimethyltetrahydroquinolines (Lions, Perkin, and Robinson), 1163.

$C_{15}H_{23}O_3N$ Ngaione oxime (McDowall), 2204.
$C_{15}H_{23}O_4N$ Veratrylideneaminoacetal (Forsyth, Kelly, and Pyman), 1665.
$C_{15}H_{25}O_4N$ Veratrylaminoacetal (Forsyth, Kelly, and Pyman), 1665.
$C_{15}H_{26}O_2Te$ 2-*n*-Decyl*cyclo*telluropentane-3:5-dione (Morgan and Taylor), 2620.

15 IV

$C_{15}H_7O_2NCl_4$ Tetrachlorophthal-*p*-tolil (Brady, Quick, and Welling), 2267.
$C_{15}H_9ONCl_6$ 2:4-Di(trichloromethyl)benzanilide (Perkin and Stone), 2296.
$C_{15}H_{10}O_3N_3Cl_3$ Acetyl-*m*-nitrobenzaldehydetrichlorophenylhydrazone (Chattaway and Walker), 1697.
$C_{15}H_{10}O_3N_3Br_3$ Acetyl-*m*-nitrobenzaldehydetribromophenylhydrazone (Chattaway and Walker), 1697.
$C_{15}H_{10}O_4N_3Cl_3$ α-Acetyl-β-nitrobenzoyltrichlorophenylhydrazines (Chattaway and Walker), 1693.
$C_{15}H_{10}O_4N_3Br_3$ α-Acetyl-β-nitrobenzoyltribromophenylhydrazine (Chattaway and Walker), 1696.
$C_{15}H_{11}ONCl_4$ 2:4-Di(dichloromethyl)benzanilide (Perkin and Stone), 2291.
$C_{15}H_{11}O_4N_3Cl_2$ α-Acetyl-β-nitrobenzoylchlorophenylhydrazines (Chattaway and Walker), 1693.
$C_{15}H_{11}O_4N_3Br_2$ α-Acetyl-β-nitrobenzoyldibromophenylhydrazines (Chattaway and Walker), 1696.
$C_{15}H_{12}O_4N_3Cl$ α-Acetyl-β-*p*-nitrobenzoyl-*p*-chlorophenylhydrazine (Chattaway and Walker), 1693.
$C_{15}H_{12}O_4N_3Br$ α-Acetyl-β-nitrobenzoylbromophenylhydrazines (Chattaway and Walker), 1696.
$C_{15}H_{12}N_2Br_2S$ Dibromo-1-toluidinomethylbenzthiazoles, and their salts (Hunter), 2026.
$C_{15}H_{14}N_2Br_4S$ 1-*p*-Toluidino-5-methylbenzthiazole tetrabromide (Hunter), 2027.
$C_{15}H_{14}N_2Br_6S$ 1-*o*-Toluidino-3-methylbenzthiazole hexabromide (Hunter), 2026.
$C_{15}H_{14}O_9N_3As$ Dinitro-4′-ethoxybenzoyl-4-aminophenylarsinic acids (King and Murch), 2646.
$C_{15}H_{15}O_6N_2As$ 3′-Acetylamino-4′-hydroxybenzoyl-4-aminophenylarsinic acid (King and Murch), 2651.
$C_{15}H_{15}O_7N_2As$ 3′-Nitro-4′-ethoxybenzoyl-4-aminophenylarsinic acid (King and Murch), 2646.
$C_{15}H_{15}N_2Br_7S$ 1-*m*-Toluidino-*m*-toluthiazole hexabromide hydrobromide (Hunter), 2027.
$C_{15}H_{16}OIAs$ 10-Methyl-10-ethylphenoxarsonium iodide (Aeschlimann), 814.
$C_{15}H_{17}O_2NS$ *p*-Toluenesulphonbenzylmethylamide (Holmes and Ingold), 1813.
$C_{15}H_{17}O_5N_2As$ 3′-Amino-4′-ethoxybenzoyl-4-aminophenylarsinic acid, and its salts (King and Murch), 2646.
$C_{15}H_{26}O_2Cl_2Te$ 2-*n*-Decyl*cyclo*telluripentane-3:5-dione 1:1-dichloride (Morgan and Taylor), 2620.

C_{16} Group.

$C_{16}H_{16}$ αγ-Diphenyl-γ-methyl-Δ$^{\alpha}$-propene (Trotman), 92.
$C_{16}H_{18}$ αγ-Diphenyl-β-methylpropane (Trotman), 93.

16 II

$C_{16}H_{10}N_2$ 1:6-Naphthadiquinoline (Armit and Robinson), 1614.
$C_{16}H_{12}O_3$ 7-Hydroxy-4-benzylcoumarin (Baker and Robinson), 1984.
7-Hydroxy-2-methyl*iso*flavone (Baker and Robinson), 1984.
7-Methoxy*iso*flavone (Baker and Robinson), 1986.

$C_{16}H_{12}O_4$ 5:7-Dihydroxy-2-methyl*iso*flavone (BAKER and ROBINSON), 1984.
7:8-Dihydroxy-3-phenyl-2-methylbenzo-γ-pyrone (BAKER), 2357.
$C_{16}H_{12}O_5$ Anthrapurpurin dimethyl ether (MILLER and PERKIN), 2690.
Galangin methyl ether (KALFF and ROBINSON), 182.
$C_{16}H_{12}O_7$ Quercetin methyl ether, and its potassium salt (KUBOTA and PERKIN), 1894.
$C_{16}H_{14}O_3$ 4-Methoxyphenyl benzyl diketone (MALKIN and ROBINSON), 375.
Phenyl 4-methoxybenzyl diketone (MALKIN and ROBINSON), 374.
$C_{16}H_{14}O_5$ Homopiperonylresacetophenone (BAKER and ROBINSON), 1430.
$C_{16}H_{16}O_3$ Benzylorcacetophenone (BAKER), 2356.
$C_{16}H_{16}O_4$ Methoxybenzylmandelic acids (MALKIN and ROBINSON), 376.
$C_{16}H_{17}N$ 1-Benzyl-1:2:3:4-tetrahydro*iso*quinoline, and its salts (FORSYTH, KELLY, and PYMAN), 1664.
$C_{16}H_{17}Br$ β-Bromo-α-phenyl-β-benzylpropane (TROTMAN), 92.
$C_{16}H_{18}O$ Dibenzylmethylcarbinol (TROTMAN), 92.
$C_{16}H_{18}O_2$ α-Hydroxy-β-methoxy-αγ-diphenylpropane (MALKIN and ROBINSON), 377.
$C_{16}H_{18}O_4$ Lactone, from ethyl sodio*iso*propylmalonate and phenacyl bromide (R. M. and J. N. RÂY), 2723.
$C_{16}H_{18}O_6$ Ethyl β-methylpimelate-β-acetate (FARMER and ROSS), 2363.
$C_{16}H_{19}As$ Phenylmesitylmethylarsine (HUNT and TURNER), 2669.
$C_{16}H_{20}N_2$ Diphenyl-βγ-diamino-*n*-butanes (MORGAN and SKINNER), 1734.
$C_{16}H_{24}O_8$ Ethyl *cyclo*butane-1:2:2:3-tetracarboxylate (ING and PERKIN), 2394.
$C_{16}H_{26}O_2$ Caryophyllene formate (ROBERTSON, KERR, and HENDERSON), 1945.
Ngaiol acetate (MCDOWALL), 2205.
$C_{16}H_{26}O_3$ Ngaiol methyl ether (MCDOWALL), 2206.
$C_{16}H_{30}O_2$ *n*-Tridecoylacetone, and its copper salt (MORGAN and HOLMES), 2894.
$C_{16}H_{30}O_3$ 4-Ketopalmitic acid (G. M. and R. ROBINSON), 180.
$C_{16}H_{32}O_2$ Palmitic acid, sodium salt, equilibria of, with water and sodium chloride (MCBAIN and LANGDON), 852.

16 III

$C_{16}H_{12}O_3N_2$ 6′-Aminopiperonylideneoxindole (ARMIT and ROBINSON), 1612.
$C_{16}H_{12}Cl_3As$ αα′-Dichlorodistyrylchloroarsine (HUNT and TURNER), 998.
$C_{16}H_{13}ON_2$ 2-Styryl-1-methyl-4-quinazolone (HEILBRON, KITCHEN, PARKES, and SUTTON), 2172.
$C_{16}H_{13}O_2N_3$ 2:3-Dimethoxyindophenazine, and its salts (ARMIT and ROBINSON), 1615.
$C_{16}H_{13}O_3Cl$ 5:7-Dihydroxy-2-phenyl-4-methylbenzopyrylium chloride, and its ferrichloride (WALKER and HEILBRON), 687.
$C_{16}H_{13}O_4Cl$ Galanginidin chloride 3-methyl ether ($+H_2O$) (MALKIN and ROBINSON), 1192.
$C_{16}H_{13}O_8N_3$ 2:4:6-Trinitro-3′:4′-dimethoxystilbene (GULLAND and ROBINSON), 1503.
$C_{16}H_{14}O_2Br_2$ Phenyl αβ-dibromo-α-methoxy-β-phenylethyl ketone (MALKIN and ROBINSON), 372.
$C_{16}H_{14}O_6N_2$ Dinitrodimethoxystilbenes (GULLAND and ROBINSON), 1502.
$C_{16}H_{14}O_7N_2$ Benzoyl derivative of trimethylene glycol monodinitrophenyl ether (FAIRBOURNE and FOSTER), 2762.
$C_{16}H_{15}O_3N$ Ethyl phenyl-4-pyridylpyruvate (SINGH), 2448.
$C_{16}H_{16}O_2N_2$ Benzildioxime dimethyl ethers (BRADY and PERRY), 2879.
Benzoyl-*p*-dimethylamino-α-benzaldoxime (BRADY and MCHUGH), 2421.
p-Dimethylaminobenzylidene-*p*-aminobenzoic acid (WAYNE and COHEN), 460.
Phenylpyruvic acid *p*-tolylhydrazone (WALKER), 1862.

$C_{16}H_{16}O_4N_2$ 2-Nitro-4-amino-2′:3′-dimethoxystilbene (Gulland and Robinson), 1502.

$C_{16}H_{17}ON$ Acetodibenzylamide (Holmes and Ingold), 1819.

$C_{16}H_{17}O_2N$ *p*-Dimethylaminodiphenylacetic acid (Singh), 2447.

$C_{16}H_{17}O_3N$ *p*-Dimethylaminobenzilic acid (Singh), 2447.

$C_{16}H_{18}O_2Te_2$ Bis-*p*-phenetyl ditelluride (Morgan and Drew), 2311.

$C_{16}H_{18}O_4Te_2$ Bis-1:3-dimethoxyphenyl 4:4-ditelluride (Morgan and Drew), 2313.

$C_{16}H_{19}O_4N$ Divanillylamine, and its hydrochloride (Jones and Pyman), 2596.

$C_{16}H_{20}O_4N_2$ Ethyl β-carbethoxy-γ-benzeneazo-Δβ-pentenoate (Macbeth and Traill), 1120.

$C_{16}H_{21}O_4N$ Ethyl *p*-dimethylaminobenzylidenemalonate (Wayne and Cohen), 459.

$C_{16}H_{25}O_3N_3$ Ngaione semicarbazone (McDowall), 2204.

$C_{16}H_{27}O_3N$ β-*p*-Ethoxyanilinobutaldehyde diethylacetal (Mason), 1034.

$C_{16}H_{32}N_2S$ γγ′-Dipiperidinodipropyl sulphide, and its picrate (Bennett and Hock), 2676.

16 IV

$C_{16}H_{10}OClAs$ 7-Chloro-αβ-naphthaphenoxarsine (Aeschlimann), 814.

$C_{16}H_{15}O_9N_2As$ 3′-Nitro-4′-ethylcarbonatobenzoyl-4-aminophenylarsinic acid (King and Murch), 2649.

$C_{16}H_{16}O_3BrAs$ 10-Carboxymethyl-10-ethylphenoxarsonium bromide (Aeschlimann), 814.

$C_{16}H_{17}O_2N_2Cl$ Anisylideneazine hydrochloride, and its reaction with stannic chloride (Shoesmith and Slater), 1490.

$C_{16}H_{17}O_4NS$ Toluene-*p*-sulphonylbenzylaminoacetic acid (Clemo and Perkin), 2307.

$C_{16}H_{17}O_6N_2As$ 3′-Acetylamino-4′-anisoyl-4-aminophenylarsinic acid (King and Murch), 2642.

$C_{16}H_{18}OIAs$ 10:10-Diethylphenoxarsonium iodide (Aeschlimann), 814.

$C_{16}H_{18}O_2Cl_2Te$ Bis-*p*-phenetyltelluridichloride (Morgan and Drew), 2312.

$C_{16}H_{18}O_4Cl_2Te$ Bis-1:3-dimethoxyphenyl-4-telluridichloride (Morgan and Drew), 2313.

$C_{16}H_{25}O_2N_3S$ Ngaione thiosemicarbazone, and its silver salt (McDowall), 2203.

C_{17} Group.

$C_{17}H_{20}$ α-Phenyl-β-benzyl-β-methylpropane (Trotman), 94.

17 II

$C_{17}H_{10}O_3$ *iso*Benzalizarin (Miller and Perkin), 2690.

$C_{17}H_{12}O_4$ 3:7-Dihydroxy-2-styrylchromone (Robinson and Shinoda), 1975.

$C_{17}H_{12}O_5$ 3:5:7-Trihydroxy-2-styrylchromone (Robinson and Shinoda), 1977.

$C_{17}H_{14}O_3$ 7-Hydroxy-2-methyl*iso*flavone methyl ether (Baker and Robinson), 1984.

$C_{17}H_{14}O_4$ Dihydroxy-3-benzyl-2-methylbenzo-γ-pyrones (Baker), 2355.

3:7-Dihydroxy-2-β-phenylethylchromone (Robinson and Shinoda), 1977.

$C_{17}H_{14}O_6$ 3:4′-Dimethoxy-5:7-dihydroxyflavone (Robinson and Shinoda), 1980.

$C_{17}H_{16}O_2$ Benzylbenzoylacetone (Trotman), 94.

$C_{17}H_{16}O_3$ 4-Methoxyphenyl β-methoxystyryl ketone (Malkin and Robinson), 375.

Phenyl β:4-dimethoxystyryl ketone (Malkin and Robinson), 374.

$C_{17}H_{16}O_4$ Benzoylveratroylmethane, and its copper salt (Gulland and Robinson), 1501.

4-Methoxyphenyl 4-methoxybenzyl diketone (Malkin and Robinson), 375.

$C_{17}H_{16}O_5$ Homopiperonylpaeanol (Baker and Robinson), 1430.
$C_{17}H_{16}O_7$ 2:4-Dihydroxy-3′:4′:5′-trimethoxybenzil (Marsh and Stephen), 1637.
$C_{17}H_{16}O_8$ 2:4:6-Trihydroxy-3′:4′:5′-trimethoxybenzil (Marsh and Stephen), 1637.
$C_{17}H_{18}O$ *as*-Dibenzylacetone (Mills and Akers), 2477.
$C_{17}H_{18}O_5$ 4:4′-Dimethoxy-α-benzylmandelic acid (Malkin and Robinson), 377.
Homoveratrylresacetophenone (Baker and Robinson), 1433.
$C_{17}H_{19}N$ 2-β-Phenylethyl-1:2:3:4-tetrahydro*iso*quinoline, and its hydrochloride (Haworth, Perkin, and Pink), 1716.
$C_{17}H_{22}O_5$ Ethyl 2-ethoxy-3-phenyl*cyclo*propane-1:2-dicarboxylate (Haerdi and Thorpe), 1243.
$C_{17}H_{22}N_2$ Di(β-phenylethylamino)methane (Short), 271.
$C_{17}H_{32}O_2$ Myristoylacetone, and its copper salt (Morgan and Holmes), 2894.
$C_{17}H_{32}O_3$ Ethyl 2-acetyl-*n*-tridecoate (G. M. and R. Robinson), 179.

17 III

$C_{17}H_{12}O_2N_2$ 10:11-Anhydro-7:8-methylenedioxyquinindoline 10-methohydroxide (Armit and Robinson), 1613.
$C_{17}H_{13}ON$ Oxy*iso*protoberberine (Haworth, Perkin, and Pink), 1717.
$C_{17}H_{13}O_2N_3$ α-Naphthaldehyde *p*-nitrophenylhydrazone (Stephen), 1877.
$C_{17}H_{13}O_3N$ Coumarincarboxylic acid *p*-toluidide (Wayne and Cohen), 457.
$C_{17}H_{13}O_6N_3$ Acetyl-4-aldehydo-1:2-hydroxyphthalide *p*-nitrophenylhydrazone (Perkin and Stone), 2293.
$C_{17}H_{15}ON$ 3-Benzylidene-4-keto-6-methyl-1:2:3:4-tetrahydroquinoline (Clemo and Perkin), 2305.
$C_{17}H_{15}O_2N$ 2-β-Phenylethylhomophthalimide (Haworth, Perkin, and Pink), 1715.
$C_{17}H_{18}O_2N_2$ Malonmonobenzylmono-*p*-tolylamide (West), 751.
$C_{17}H_{15}O_2N_3$ 2:3-Dimethoxy-5(or 11)-methyl*iso*indophenazine (Armit and Robinson), 1616.
$C_{17}H_{15}O_5Cl$ Datiscetinidin chloride 3:2′-dimethyl ether (Pratt and Robinson), 1185.
5:7-Dihydroxy-3:3′-dimethoxyflavylium chloride ($+H_2O$) (Pratt and Robinson), 1186.
Pelargonidin chloride 3:4′-dimethyl ether (Malkin and Robinson), 1194.
Pelargonidin chloride 3:3′-dimethyl ether (Pratt and Robinson), 1187.
$C_{17}H_{17}ON$ 2-β-Phenylethyl-3:4-dihydro-1-*iso*quinolone (Haworth, Perkin, and Pink), 1715.
$C_{17}H_{17}ON_3$ 2-Benzyl-1-hydrindone semicarbazone (Mills and Akers), 2478.
$C_{17}H_{17}O_3N$ *N*-β-Phenylethylhomophthalamic acid (Haworth, Perkin, and Pink), 1716.
$C_{17}H_{17}O_3N_3$ Benzylidene-δ-3-carbethoxyphenylsemicarbazide (Wilson and Crawford), 107.
2:3-Dimethoxy-5(or 11)-methyl*iso*indophenazine methohydroxide (Armit and Robinson), 1616.
$C_{17}H_{18}O_4N_2$ Nitro-3-methoxy-2-ethoxybenzylidene-*p*-toluidines (Rubenstein), 2268.
$C_{17}H_{20}ON_2$ β-*o*-Toluidinopropiono-*o*-toluidide (Clemo and Perkin), 2303.
$C_{17}H_{21}O_5N$ Carboxycamphoranilic acids, and their molecular rotation (M. and R. Singh), 1966.
$C_{17}H_{22}IAs$ Phenylmesityldimethylarsonium iodide (Hunt and Turner), 2669.
$C_{17}H_{23}O_2N$ Benzoylmenthoneoximes (Read and Cook), 2786.
$C_{17}H_{24}O_4N_2$ 6-Acetylamino-1-acetyl-5:8-dimethoxy-2:4-dimethyl-1:2:3:4-tetrahydroquinoline (Lions, Perkin, and Robinson), 1163.
$C_{17}H_{26}O_3S_2$ Ngaiol methyl xanthate (McDowall), 2205.

17 IV

$C_{17}H_{14}ONBr$ 3-Benzylidene-4-keto-6-methyl-1:2:3:4-tetrahydroquinoline bromide (Clemo and Perkin), 2305.

$C_{17}H_{14}O_2Cl_5Fe$ 3-Chloro-8-ethoxy-2-phenylbenzopyrylium ferrichloride (Ridgway and Robinson), 767.

$C_{17}H_{15}O_4SAs$ Sulphophenyl-α-naphthylmethylarsine oxide (Aeschlimann), 813.

$C_{17}H_{17}O_2N_2Br$ Bromomalonmonobenzylmono-*p*-tolylamide (West), 751.

Bromomalon-*p*-toluidide (West), 752.

$C_{17}H_{17}O_3NS$ Toluene-*p*-sulphonyl-4-ketomethyl-1:2:3:4-quinolines (Clemo and Perkin), 2303.

$C_{17}H_{17}O_4NS$ Toluene-*p*-sulphonyl-6-methoxy-4-keto-1:2:3:4-tetrahydroquinoline (Clemo and Perkin), 2305.

$C_{17}H_{17}O_7N_2As$ 3′-Acetylamino-4′-acetoxybenzoyl-4-aminophenylarsinic acid (King and Murch), 2651.

$C_{17}H_{19}O_4NS$ Toluene-*p*-sulphonyl-β-toluidinopropionic acids (Clemo and Perkin), 2302.

$C_{17}H_{19}O_5NS$ Toluene-*p*-sulphonyl-β-*p*-anisidinopropionic acid (Clemo and Perkin), 2305.

$C_{17}H_{19}O_7N_2As$ 3′-Carbethoxyamino-4′-anisoyl-4-aminophenylarsinic acid (King and Murch), 2642.

$C_{17}H_{27}O_2N_2I$ Dehydroseretholemethine methiodide (Stedman and Barger), 254.

17 V

$C_{17}H_{10}O_3NBrS$ Colouring matter, from isatin and 4-bromo-2-carboxy-5-methoxyphenylthiolacetic acid (Griffith and Hope), 995.

$C_{17}H_{16}O_3NClS$ Toluene-*p*-sulphonyl-3-chloro-4-ketomethyl-1:2:3:4-tetrahydroquinolines (Clemo and Perkin), 2304.

Toluene-*p*-sulphonyl-3-chloro-6-methoxydihydroquinoline (Clemo and Perkin), 2306.

C_{18} Group.

$C_{18}H_{12}O_3$ *n*- and *iso*-Benzalizarin methyl ethers (Miller and Perkin), 2689.

$C_{18}H_{12}O_7$ Diacetylanthragallol (Kubota and Perkin), 1893.

$C_{18}H_{14}O_3$ *r*-Phenyl-α-naphthylglycollic acid, conversion of, into ketones, and its silver salt (McKenzie and Tattersall), 2522.

$C_{18}H_{14}O_4$ 7-Hydroxy-3-methoxy-2-styrylchromone (Robinson and Shinoda), 1975.

Acetyl derivative of 7-hydroxy-2-methyl*iso*flavone (Baker and Robinson), 1984.

$C_{18}H_{14}O_5$ 7-Hydroxy-3-homopiperonyl-2-methylchromone (Baker and Robinson), 1431.

3-Methoxy-5:7-dihydroxy-2-styrylchromone (Robinson and Shinoda), 1977.

$C_{18}H_{14}O_6$ 2:4-Diacetoxybenzil (Marsh and Steven), 1636.

$C_{18}H_{16}O_4$ 7-Hydroxy-3-methoxy-2-β-phenylethylchromone (Robinson and Shinoda), 1976.

$C_{18}H_{16}O_6$ 3:7:2′-Trimethoxy-5-hydroxyflavone (Kalff and Robinson), 1971.

$C_{18}H_{16}N_4$ 10:15-Diamino-1:8-dimethyldibenzocopyrine, and its hydrochloride (Gulland and Robinson), 1500.

$C_{18}H_{18}O_3$ β-Phenylpropionic anhydride (Robinson and Shinoda), 1976.

$C_{18}H_{18}O_4$ 4-Methoxyphenyl β:4-dimethoxystyryl ketone (Malkin and Robinson), 375.

$C_{18}H_{18}O_5$ 4:4′-Dicarboxy-3:3′-dimethyldibenzyl ether (Perkin and Stone), 2286.

$C_{18}H_{20}O_5$ Camphoryl hydrogen phthalates (Forster and Shukla), 1859.

$C_{18}H_{32}O_{10}$ Di(trimethyl glucosan) (Irvine and Oldham), 2919.

$C_{18}H_{34}O_2$ Oleic acid, synthesis of (G. M. and R. Robinson), 175; oxidation of (Lapworth and Mottram), 1628, 1987.

n-Pentadecoylacetone, and its copper salt (Morgan and Holmes), 2894.

$C_{18}H_{34}O_3$ Lactarinic acid (G. M. and R. Robinson), 179.

$C_{18}H_{36}O_4$ Dihydroxystearic acid, oxidation of (Lapworth and Mottram), 1987.

18 III

$C_{18}H_{11}O_5N$ 6:7:3′:4′-Bismethylenedioxy-9-ketoprotopapaverine, and its salts (Buck, Perkin, and Stevens), 1470.

$C_{18}H_{12}OCl_2$ Phenyl-α-naphthylchloroacetyl chloride (McKenzie and Tattersall), 2526.

$C_{18}H_{12}O_5N_2$ Oxime of 6:7:3′:4′-bismethylenedioxy-9-ketoprotopapaverine (Buck, Perkin, and Stevens), 1471.

$C_{18}H_{13}OCl$ Phenyl-α-naphthylacetyl chloride (McKenzie and Tattersall), 2527.

$C_{18}H_{13}O_3N$ 2:3-Methylenedioxyoxyprotoberberines (Haworth, Perkin, and Pink), 1718.

$C_{18}H_{13}O_4N$ 6:7:3′:4′-Bismethylenedioxyprotopapaverine, synthesis of, and its picrate (Buck, Perkin, and Stevens), 1462.

$C_{18}H_{13}O_5N$ 6:7:3′:4′-Bismethylenedioxy-9-hydroxyprotopapaverine (Buck, Perkin, and Stevens), 1471.

6:7:3′:4′-Bismethylenedioxy-9-keto-3:4-dihydroprotopapaverine, and its salts (Buck, Perkin, and Stevens), 1470.

$C_{18}H_{14}O_5N_2$ Oxime of 6:7:3′:4′-bismethylenedioxy-9-keto-3:4-dihydroprotopapaverine (Buck, Perkin, and Stevens), 1470.

$C_{18}H_{15}O_2N$ 2:3-Methylenedioxydihydroprotoberberine, and its salts (Haworth, Perkin, and Pink), 1722.

$C_{18}H_{15}O_3Cl$ 4′:7-Dihydroxy-2-styryl-4-methylbenzopyrylium chloride (Heilbron, Walker, and Buck), 692.

$C_{18}H_{15}O_3N$ 2:3-Methylenedioxyoxydihydro*iso*protoberberine (Haworth, Perkin, and Pink), 1719.

$C_{18}H_{15}O_4N$ 6:7:3′:4′-Bismethylenedioxy-3:4-dihydroprotopapaverine, and its picrate (Buck, Perkin, and Stevens), 1466.

2-Homopiperonylhomophthalimide (Haworth, Perkin, and Pink), 1717.

$C_{18}H_{15}O_4Cl$ 3′:4′:7-Trihydroxy-2-styryl-4-methylbenzopyrylium chloride (Heilbron, Walker, and Buck), 693.

$C_{18}H_{15}O_5N$ Nitro-3′:4′-dimethoxy-2-benzylidene-1-hydrindone (Lions, Perkin, and Robinson), 1168.

$C_{18}H_{15}BrGe$ Triphenylgermanium bromide (Morgan and Drew), 1763.

$C_{18}H_{16}O_2N_2$ 4′-Methoxy-2-styryl-3-methyl-4-quinazolone (Heilbron, Kitchen, Parkes, and Sutton), 2171.

$C_{18}H_{16}O_2S_2$ 2:4-Xylyl 2-naphthalenethiolsulphonate (Gibson, Miller, and Smiles), 1824.

$C_{18}H_{16}O_3S_2$ 6-Methoxy-3-tolyl 2-naphthalenethiolsulphonate (Gibson, Miller, and Smiles), 1824.

$C_{18}H_{17}O_2N$ 2:3-Methylenedioxytetrahydroprotoberberines, and their salts (Haworth, Perkin, and Pink), 1718.

$C_{18}H_{17}O_3Cl$ 5:7-Dimethoxy-2-phenyl-4-methylbenzopyrylium chloride, and its ferrichloride (Walker and Heilbron), 688.

$C_{18}H_{17}O_4N$ 6:7:3′:4′-Bismethylenedioxy-1:2:3:4-tetrahydroprotopapaverine, and its salts (Buck, Perkin, and Stevens), 1467.

Piperonylidene-γ-piperonylpropylamine (Baker and Robinson), 1429.

$C_{18}H_{17}O_5N$ *N*-Homopiperonylhomophthalamic acid (Haworth, Perkin, and Pink), 1718.

$C_{18}H_{17}O_5Cl$ Fisetinidin chloride trimethyl ether ($+2H_2O$) (Pratt and Robinson), 170.

$C_{18}H_{17}O_6Cl$ Cyanidin chloride 3:3′:4′-trimethyl ether ($+1\frac{1}{2}H_2O$) (Pratt and Robinson), 1189.

Morinidin chloride 3:2′:4′-trimethyl ether (Pratt and Robinson), 1188.

$C_{18}H_{18}O_2N_4$ Acetophenoneoxalyldihydrazone (Wilson and Pickering), 966.

$C_{18}H_{18}O_4N_2$ *N*-Homopiperonylhomophthalamic acid amide (Haworth, Perkin, and Pink), 1718.

$C_{18}H_{18}O_6N_6$ $\alpha\gamma$-Dialdehydopropane-β-carboxylic acid di-*p*-nitrophenylhydrazone (Perkin and Pink), 194.

$C_{18}H_{19}O_2N$ Benzylhydrohydrastinine, and its hydrochloride (Haworth, Perkin, and Pink), 1721.

$C_{18}H_{19}O_3N$ Methyl *N*-β-phenylethylhomophthalamate (Haworth, Perkin, and Pink), 1716.

$C_{18}H_{19}O_3N_3$ 2:3-Dimethoxy-6-methylindophenazine methohydroxide (Armit and Robinson), 1616.

$C_{18}H_{20}O_2N_2$ Ethyl phenylpyruvate *p*-tolylhydrazone (Walker), 1862.

$C_{18}H_{20}O_4N_2$ 5-Nitro-2:3-diethoxybenzylidene-*p*-toluidine (Rubenstein), 2269.

$C_{18}H_{21}O_3N$ Ethyl *p*-dimethylaminobenzilate (Singh), 2446.

1-1′-Hydroxy*cyclo*pentane-1′-carboxylylanilino*cyclo*pentane-1-carboxylactone (Plant and Facer), 2039.

$C_{18}H_{21}O_6Br$ Ethyl α-carbethoxy-α'-bromo-β-phenylglutaconate (Haerdi and Thorpe), 1245.

$C_{18}H_{22}O_2S$ $\gamma\gamma'$-Diphenoxydipropyl sulphide (Bennett and Hock), 2675.

$C_{18}H_{23}O_3N$ Ethyl 3-*p*-dimethylaminophenyl-5-methyl-Δ^5-*cyclo*hexen-1-one-2-carboxylate (Heilbron, Forster, and Whitworth), 2165.

$C_{18}H_{25}O_4N$ Ethyl 3-*p*-dimethylaminophenyl-5-methyl*cyclo*hexan-5-ol-1-one-2-carboxylate (Heilbron, Forster, and Whitworth), 2165.

$C_{18}H_{26}O_6$ Ethyl Δ^1-*cyclo*hexene-1-acetate-2-malonate (Baker), 988.

$C_{18}H_{27}ON_3$ Benzylidene-δ-menthylsemicarbazide (Wilson and Crawford), 106.

$C_{18}H_{27}O_3N$ 9-Carbethoxynonanilide (G. M. and R. Robinson), 177.

$C_{18}H_{37}ON$ Acetohexadecylamide (Adam and Dyer), 73.

18 IV

$C_{18}H_{10}O_4S_2Br_2$ 5:5′-Dibromo-6:6′-dimethoxy-2:2′-bisoxythionaphthen (Griffith and Hope), 990.

$C_{18}H_{14}O_2NI$ 2:3-Methylenedioxyprotoberberinium iodide (Haworth, Perkin, and Pink), 1722.

$C_{18}H_{14}O_3NCl$ 3-Chloro-2-homopiperonyl-1-*iso*quinolone (Haworth, Perkin, and Pink), 1717.

$C_{18}H_{16}O_3Cl_5Fe$ 3-Chloro-4′-methoxy-8-ethoxy-2-phenylbenzopyrylium ferrichloride (Ridgway and Robinson), 768.

$C_{18}H_{18}O_7N_2S$ 6′-Methylaminopiperonylideneoxindole methyl hydrogen sulphate (Armit and Robinson), 1612.

$C_{18}H_{19}O_4NS$ Toluene-*p*-sulphonyl-6-ethoxy-4-keto-1:2:3:4-tetrahydroquinoline (Clemo and Perkin), 2306.

$C_{18}H_{20}O_2N_2S_2$ 2:2′-Diacetylmethylaminodiphenyl disulphide (Clark), 974.

$C_{18}H_{21}O_4NS$ Ethyl toluene-*p*-sulphonylbenzylaminoacetate (Clemo and Perkin), 2307.

$C_{18}H_{21}O_5NS$ Toluene-*p*-sulphonyl-β-*p*-phenetidinopropionic acid (Clemo and Perkin), 2306.

C_{19} Group.

$C_{19}H_{12}O_4$ Acetyl*iso*benzalizarin (Miller and Perkin), 2689.

$C_{19}H_{16}O$ Phenyl-α-naphthylacetone (McKenzie and Tattersall), 2528.

$C_{19}H_{16}O_5$ 1-Acetoxy-2-methoxyanthrone (Miller and Perkin), 2688.
7-Hydroxy-3-homopiperonyl-2-methylchromone methyl ether (Baker and Robinson), 1432.

$C_{19}H_{16}O_6$ 3:4′-Dimethoxy-5:7-dihydroxy-2-styrylchromone (Robinson and Shinoda), 1978.

$C_{19}H_{16}O_7$ Diacetoxymethoxybenzils (Marsh and Stephen), 1636.

$C_{19}H_{18}O_5$ 7-Hydroxy-3-homoveratryl-2-methylchromone (Baker and Robinson), 1433.

$C_{19}H_{18}O_8$ 3:3′:4′:5′-Tetramethylmyricetin (Kalff and Robinson), 183.

$C_{19}H_{18}N_2$ *p*-Dimethylaminobenzylidene-β-naphthylamine (Wayne and Cohen), 460.

$C_{19}H_{20}O_2$ 3:3-Dibenzylacetylacetone (Morgan and Taylor), 802.

$C_{19}H_{26}O_8$ Ethyl diacetalmalonate (Perkin and Pink), 192.

$C_{19}H_{36}O_2$ Palmitoylacetone, and its copper salt (Morgan and Holmes), 2895.

$C_{19}H_{38}O_6$ Acid, and its derivatives, from saponification of cutin (Legg and Wheeler), 1419.

19 III

$C_{19}H_{13}O_5N$ Bismethylenedioxyoxyprotoberberine (Buck, Perkin, and Stevens), 1469.

$C_{19}H_{13}N_2Cl_3$ Benzophenone-2:4:6-trichlorophenylhydrazone (Humphries, Humble, and Evans), 1306.

$C_{19}H_{14}O_4N$ 2:3:10:11-Bismethylenedioxyprotoberberine, synthesis of, and its salts (Buck, Perkin, and Stevens), 1468.

$C_{19}H_{14}N_2Cl_2$ Benzophenone-2:4-dichlorophenylhydrazone (Humphries, Humble, and Evans), 1306.

$C_{19}H_{14}N_4Br_2$ Dibromoformazylbenzene (Chattaway and Walker), 982.

$C_{19}H_{15}ON$ *N*-Phenylbenziminophenyl ether, molecular rearrangement of (Chapman), 1992.

$C_{19}H_{15}ON_3$ 1-Keto-2-phenyl-3:5-dimethyl-1:2-dihydro-2:4:6-naphtha*iso*triazine (Gulland and Robinson), 1498.

$C_{19}H_{15}O_2N$ *o*-Benzoylaminodiphenyl ether (Turner and Sheppard), 546.

$C_{19}H_{15}O_4N$ Bismethylenedioxydihydroprotoberberine, and its picrate (Buck, Perkin, and Stevens), 1469.

$C_{19}H_{16}O_3N_2$ 1-Cyano-6:7-dimethoxy-2-benzoyl-1:2-dihydro*iso*quinoline (Haworth and Perkin), 1442.

$C_{19}H_{16}O_4N_2$ Methoxy-3′:4′-methylenedioxy-2-styryl-1-methyl-4-quinazolones (Heilbron, Kitchen, Parkes, and Sutton), 2174.

$C_{19}H_{16}O_5Br_2$ 7-Hydroxy-3-homopiperonyl-2-methylchromone methyl ether dibromide (Baker and Robinson), 1432.

$C_{19}H_{17}O_3Cl$ 7-Hydroxy-4′-methoxy-2-styryl-4-methylbenzopyrylium chloride (Heilbron, Walker, and Buck), 693.

$C_{19}H_{17}O_4N$ 2:3:10:11-Bismethylenedioxytetrahydroprotoberberine (Buck, Perkin, and Stevens), 1467.

$C_{19}H_{17}O_4Cl$ 4′:7-Dihydroxy-3′-methoxy-4-styryl-2-methylbenzopyrylium chloride (Heilbron, Walker, and Buck), 693.

$C_{19}H_{18}O_2Te$ 4:4-Dibenzyl*cyclo*telluropentane-3:5-dione (Morgan and Taylor), 803.

$C_{19}H_{18}O_3N_2$ 3′:4′-Dimethoxy-2-styryl-3-methyl-4-quinazolone (Heilbron, Kitchen, Parkes, and Sutton), 2171.

$C_{19}H_{18}O_8N_6$ αγ-Dialdehydopropane-ββ-dicarboxylic acid di-*p*-nitrophenylhydrazone (Perkin and Pink), 193.

$C_{19}H_{19}O_2N$ 2-β-Phenylethyl-4:4-dimethylhomophthalimide (Haworth, Perkin, and Pink), 1715.

$C_{19}H_{19}O_5N$ Methyl *N*-homopiperonylhomophthalamate (Haworth, Perkin, and Pink), 1718.

$C_{19}H_{19}O_7Cl$ Delphinidin chloride 3:3′:4′:5′-tetramethyl ether (Pratt and Robinson), 1189.

$C_{19}H_{20}O_6N_2$ 6′-Nitroveratrylnorhydrohydrastinine (Haworth and Perkin), 1450.

$C_{19}H_{20}NI$ Benzylquinaldine ethiodide (Mills and Raper), 2474.

$C_{19}H_{21}O_4N$ Methyl β-toluidinobenzylmalonates (Wayne and Cohen), 459.

$C_{19}H_{26}O_9N_4$ 4-Carbethoxybispiperidinium-1:1′-spiran picrate (Mills and Bains), 2506.

19 IV

$C_{19}H_{12}ON_2S_2$ Substance, from distyryl ketone and thiocyanogen (Challenger and Bott), 1041.

$C_{19}H_{14}ONCl$ *N*-Phenylbenziminochlorophenyl ethers (Chapman), 1996.

$C_{19}H_{18}O_2Cl_2Te$ 4:4-Dibenzyl*cyclo*telluripentane-3:5-dione 1:1-dichloride (Morgan and Taylor), 802.

$C_{19}H_{19}O_5NBr$ 6′-Bromohomoveratroylhomopiperonylamine (Haworth and Perkin), 1451.

$C_{19}H_{19}O_5Cl_4Fe$ 5:7:2′:4′-Tetramethoxyflavylium ferrichloride (Pratt and Robinson), 1134.

$C_{19}H_{20}O_4NBr$ 6′-Bromoveratrylnorhydrohydrastinine, and its salts (Haworth and Perkin), 1452.

$C_{19}H_{28}O_2NBr$ 4-Phenyl-4′-carbethoxybispiperidinium-1:1′-spiran bromides (Mills and Warren), 2512.

$C_{19}H_{28}O_2NI$ 4-Phenyl-4′-carbethoxybispiperidinium-1:1′-spiran iodides (Mills and Warren), 2512.

C_{20} Group.

$C_{20}H_{14}O_4$ Acetylbenzalizarin methyl ether (Miller and Perkin), 2689.

$C_{20}H_{14}O_8$ Triacetylanthragallol (Kubota and Perkin), 1893.

$C_{20}H_{16}O_6$ 7-Acetoxy-3-homopiperonyl-2-methylchromone (Baker and Robinson), 1431.

5:7-Diacetoxy-2-methyl*iso*flavone (Baker and Robinson), 1985.

7:8-Diacetoxy-3-phenyl-2-methylbenzo-γ-pyrone (Baker), 2357.

$C_{20}H_{16}O_7$ Diacetylgalangin 3-methyl ether (Kalff and Robinson), 182.

2-*o*-Methoxybenzylidene-4:6-diacetoxycoumaranone (Kalff and Robinson), 1969.

$C_{20}H_{16}O_8$ 2:4:6-Triacetoxybenzil (Marsh and Stephen), 1631.

$C_{20}H_{16}N_2$ Dimethyl-2:2′-diquinolyls, and their salts (Conolly), 2083.

$C_{20}H_{18}O_4$ 7-Acetoxy-3-benzyl-2:5-dimethylbenzo-γ-pyrone (Baker), 2357.

7-Hydroxy-3-benzyl-2:5-dimethylbenzo-γ-pyrone (Baker), 2357.

Lactone from ethyl sodiobenzylmalonate and phenacyl bromide (R. M. and J. N. Rây), 2723.

$C_{20}H_{18}O_5$ 4-Methoxycinnamic anhydride (Robinson and Shinoda), 1977.

$C_{20}H_{18}O_6$ Diacetylanthrapurpurinanthranol dimethyl ether (Miller and Perkin), 2691.

3:7:4′-Trimethoxy-5-hydroxy-2-styrylchromone (Robinson and Shinoda), 1978.

$C_{20}H_{18}O_7$ 3:3′:4′-Trimethoxy-5:7-dihydroxy-2-styrylchromone ($+H_2O$) (Robinson and Shinoda), 1979.

$C_{20}H_{20}O_5$ 7-Methoxy-3-homoveratryl-2-methylchromone (Baker and Robinson), 1433.

$C_{20}H_{20}O_6$ Ethyl benzoylveratroylacetate (Gulland and Robinson), 1501.

$C_{20}H_{22}O_6$ Dibenzyl dimethoxysuccinate, rotation of (Patterson and Fulton), 2436.

$C_{20}H_{24}O_7$ Ethyl 2-benzoyl*cyclo*butane-1:2:3-tricarboxylate (Ing and Perkin), 2397.
$C_{20}H_{34}O_2$ Substance, from reduction of tagetone (Jones and Smith), 2539.
$C_{20}H_{38}O_2$ Margaroylacetone, and its copper salt (Morgan and Holmes), 2895.
$C_{20}H_{40}O_2$ Arachidic acid, synthesis of (Adam and Dyer), 70.
$C_{20}H_{43}N$ Eicosylamine, hydrochloride of (Adam and Dyer), 73.

20 III

$C_{20}H_{11}O_{15}N_7$ Picryl-3-methoxy-4-picryloxybenz*syn*aldoxime (Brady and Klein), 847.
$C_{20}H_{15}ON_3$ 2-α-4-Pyridylbenzyl-3-quinoxalone (Singh), 2449.
$C_{20}H_{15}N_2Cl$ 3-Chloro-2:2-diphenyl-1:2-dihydroquinoxaline (Ingold and Weaver), 385.
$C_{20}H_{16}O_2N_2$ α-Naphthacarbamylcinnamaldoximes (Brady and McHugh), 2426.
$C_{20}H_{16}O_7Br_2$ 2-*o*-Methoxybenzylidene-4:6-diacetoxycoumaranone dibromide (Kalff and Robinson), 1970.
$C_{20}H_{17}ON$ Substance, from *as*-diphenylethylene and nitrosobenzene, constitution of (Burkhardt, Lapworth, and Walkden), 2458.
$C_{20}H_{17}O_5N$ Oxyberberine, synthesis of (Perkin, Rây, and Robinson), 740.
$C_{20}H_{18}O_4N_2$ Iminoberberine, and its hydrochloride (Haworth, Perkin, and Pink), 1723.
$C_{20}H_{19}ON$ β-Amino-ααβ-triphenylethyl alcohols (McKenzie and Wills), 290.
$C_{20}H_{19}O_2N_3$ 7-Methoxy-4′-dimethylamino-2-styryl-1-methyl-4-quinazolone (Heilbron, Kitchen, Parkes, and Sutton), 2175.
$C_{20}H_{19}O_4N$ Anhydro-7-demethylomethylpapaverinol (Haworth and Perkin), 1458.
2-Homopiperonyl-4:4-dimethylhomophthalimide (Haworth, Perkin, and Pink), 1717.
$C_{20}H_{19}O_6N$ 2-Homopiperonyl-6:7-dimethoxyhomophthalimide (Haworth, Perkin, and Pink), 1720.
$C_{20}H_{20}O_6N_2$ 6-Nitrotetrahydroberberine (Haworth and Perkin), 1451.
$C_{20}H_{21}O_4N$ 7-Demethylomethylpapaverine (Haworth and Perkin), 1458.
dl-Dicentrine, synthesis of, and its salts (Haworth, Perkin, and Rankin), 2022.
$C_{20}H_{21}O_5N$ 7-Demethylomethylpapaverinol (Haworth and Perkin), 1457.
6:7:2′:3′-Tetramethoxy-2-benzyl-1-*iso*quinolone (Haworth and Perkin), 1439.
6:7:3′:4′-Tetramethoxy-2-benzyl-1-*iso*quinolone (Haworth, Perkin, and Rankin), 1446.
$C_{20}H_{21}O_6Cl$ Cyanidin chloride pentamethyl ether, and its hydrochloride (Pratt and Robinson), 171.
$C_{20}H_{21}O_7N$ *N*-Homopiperonyl-4:5-dimethoxyhomophthalamic acid (Haworth, Perkin, and Pink), 1720.
$C_{20}H_{22}O_2N_2$ *trans*-1-Methyl*cyclo*propane-1:2-dicarboxylic acid di-*p*-toluidide (Ingold), 396.
$C_{20}H_{22}O_6N_2$ Ethyl β-*m*-nitroanilinobenzylmalonate (Wayne and Cohen), 456.
6:7-Methylenedioxy-2′:3′-dimethoxy-2-benzyl-1-nitromethyl-1:2:3:4-tetrahydro-*iso*quinoline (Haworth and Perkin), 1441.
6′-Nitroveratrylhydrohydrastinine, and its salts (Haworth, Perkin, and Rankin), 2021.
$C_{20}H_{23}O_4N$ 1-Veratrylhydrohydrastinine, and its salts (Haworth, Perkin, and Rankin), 2020.
$C_{20}H_{23}O_5N$ 1-Hydroxy-6:7:2′:3′-tetramethoxy-2-benzyl-1:2-dihydro*iso*quinoline (Haworth and Perkin), 1438.
1-Hydroxy-6:7:3′:4′-tetramethoxy-2-benzyl-1:2-dihydro*iso*quinoline (Haworth, Perkin, and Rankin), 1445.

$C_{20}H_{23}O_5N$ 6:7:2′:3′-Tetramethoxy-2-benzyl-3:4-dihydro-1-*iso*quinolone (HAWORTH and PERKIN), 1440.

$C_{20}H_{24}O_4N_2$ 6′-Aminoveratrylhydrohydrastinine, and its salts (HAWORTH, PERKIN, and RANKIN), 2021.

$C_{20}H_{24}O_5N_2$ Nitrosoamine of 7-demethylomethyltetrahydropapaverine (HAWORTH and PERKIN), 1459.

$C_{20}H_{25}O_4N$ 7-Demethylomethyltetrahydropapaverine, and its picrate (HAWORTH and PERKIN,) 1459.

6:7:2′:3′-Tetramethoxy-2-benzyl-1:2:3:4-tetrahydro*iso*quinoline (HAWORTH and PERKIN), 1439.

6:7:3′:4′-Tetramethoxy-2-benzyl-1:2:3:4-tetrahydro*iso*quinoline (HAWORTH, PERKIN, and RANKIN), 1446.

$C_{20}H_{25}O_5N$ 1-Hydroxy-6:7:2′:3′-tetramethoxy-2-benzyl-1:2:3:4-tetrahydro*iso*quinoline, and its salts (HAWORTH and PERKIN), 1440.

$C_{20}H_{26}O_2S$ $\gamma\gamma'$-Di-*p*-tolyloxydipropyl sulphide (BENNETT and HOCK), 2675.

$C_{20}H_{28}O_8N_4$ Ethyl 6-phenylhexahydro-1:2:3:4-tetrazine-1:2:3:4-tetracarboxylate (INGOLD and WEAVER), 386.

$C_{20}H_{33}O_2N_3$ Myristaldehyde *p*-nitrophenylhydrazone (STEPHEN), 1876.

$C_{20}H_{41}ON$ Aceto-octadecylamide (ADAM and DYER), 73.

20 IV

$C_{20}H_{18}O_5NCl$ 3-Chloro-2-homopiperonyl-6:7-dimethoxy-1-*iso*quinolone (HAWORTH, PERKIN, and PINK), 1720.

$C_{20}H_{20}O_2NCl$ 7-Hydroxy-4′-dimethylamino-2-styryl-4-methylbenzopyrylium chloride (HEILBRON, WALKER, and BUCK), 693.

$C_{20}H_{20}O_5NI$ 6:7-Methylenedioxy-3′:4′-dimethoxy-1-benzoyl-3:4-dihydro*iso*quinoline methiodide (HAWORTH, PERKIN, and RANKIN), 2020.

$C_{20}H_{21}O_6Cl_4Fe$ 3:5:7:2′:4′-Pentamethoxyflavylium ferrichloride (PRATT and ROBINSON), 1137.

$C_{20}H_{22}O_4NCl$ Ethyl β-*p*-chloroanilinobenzylmalonate (WAYNE and COHEN), 457.

$C_{20}H_{22}O_4NBr$ Ethyl β-*p*-bromoanilinobenzylmalonate (WAYNE and COHEN), 457.

6:7:2′:3′-Tetramethoxy-2-benzyl*iso*quinolinium bromide (HAWORTH and PERKIN), 1437.

6:7:3′:4′-Tetramethoxy-2-benzyl*iso*quinolinium bromide (HAWORTH, PERKIN, and RANKIN), 1445.

$C_{20}H_{22}O_4NI$ 6:7:2′:3′-Tetramethoxy-2-benzyl*iso*quinolinium iodide (HAWORTH and PERKIN), 1438.

6:7:3′:4′-Tetramethoxy-2-benzyl*iso*quinolinium iodide (HAWORTH, PERKIN, and RANKIN), 1445.

1-Veratryl-6:7-methylenedioxydihydro*iso*quinoline methiodide (HAWORTH, PERKIN, and RANKIN), 2020.

$C_{20}H_{24}O_2N_2S_2$ 2:2′-Diacetylethylaminodiphenyl disulphide (CLARK), 974.

$C_{20}H_{24}O_4NCl$ 6:7:3′:4′-Tetramethoxy-2-benzyl-3:4-dihydro*iso*quinolinium chloride (HAWORTH, PERKIN, and RANKIN), 1447.

$C_{20}H_{24}O_4NI$ 6:7:2′:3′-Tetramethoxy-2-benzyl-3:4-dihydro*iso*quinolinium iodide (HAWORTH and PERKIN), 1439.

6:7:3′:4′-Tetramethoxy-2-benzyl-3:4-dihydro*iso*quinolinium iodide (HAWORTH, PERKIN, and RANKIN), 1446.

$C_{20}H_{24}O_4NI_3$ 6:7:3′:4′-Tetramethoxy-2-benzyl-3:4-dihydro*iso*quinolinium periodide (HAWORTH, PERKIN, and RANKIN), 1447.

$C_{20}H_{24}O_4NS$ $\gamma\gamma'$-Dipropyl sulphide diphenylurethane (BENNETT and HOCK), 2673.

C_{21} Group.

$C_{21}H_{14}O_3$ 7-Hydroxy-2-phenyl*iso*flavone (Baker and Robinson), 1985.

$C_{21}H_{14}O_4$ 7:8-Dihydroxy-2:3-diphenylbenzo-γ-pyrone (Baker), 2357.

$C_{21}H_{14}O_5$ Diacetyl*iso*benzalizarin (Miller and Perkin), 2690.

$C_{21}H_{14}N_2$ 2-Phenylphenanthriminazole (Sircar and Ray), 1048.

$C_{21}H_{16}N_2$ 2-Phenyl-3-benzylquinoxaline (Malkin and Robinson), 373.

$C_{21}H_{16}S_2$ Benzyl 9-anthryl disulphide (Footner and Smiles), 2889.

$C_{21}H_{18}O_6$ Diacetoxy-3-benzyl-2-methylbenzo-γ-pyrones (Baker), 2356.

$C_{21}H_{18}O_8$ Diacetoxydimethoxyflavone (Kalff and Robinson), 1971.

$C_{21}H_{18}O_9$ Triacetoxymethoxybenzils (Marsh and Stephen), 1637.

$C_{21}H_{20}O_2$ αα*β*-Triphenylpropylene α*β*-glycol (Roger), 522.

$C_{21}H_{20}O_6$ 7-Acetoxy-3-homoveratryl-2-methylchromone (Baker and Robinson), 1433.

$C_{21}H_{20}O_7$ 3:7:3′:4′-Tetramethoxy-5-hydroxy-2-styrylchromone (Robinson and Shinoda), 1979.

$C_{21}H_{20}O_9$ 2:4-Diacetoxytrimethoxybenzil (Marsh and Stephen), 1637.

$C_{21}H_{24}O_6$ *ββ*′-Dibenzyloxydiethylmalonic acid, and its salts (Bennett), 1280.

$C_{21}H_{40}O_2$ Stearoylacetone, and its copper salt (Morgan and Holmes), 2895.

21 III

$C_{21}H_{12}O_3N_2$ Nitro-2-phenylphenanthroxazoles (Sircar and Ray), 1049.

$C_{21}H_{13}O_2N$ 2′-Hydroxy-2-phenylphenanthroxazole (Sircar and Ray), 1049.

$C_{21}H_{14}O_2N_2$ 1:4-*endo*-Keto-2-keto-3:3-diphenyltetrahydroquinoxaline (Ingold and Weaver), 384.

$C_{21}H_{14}O_5N_6$ Dinitro-derivative of anhydro-2:4-dialdehydobenzoic acid diphenylhydrazone (Perkin and Stone), 2293.

$C_{21}H_{14}N_2S$ Naphthylaminonaphthathiazoles (Hunter), 2272.

$C_{21}H_{16}ON_4$ Anhydro-2:4-dialdehydobenzoic acid diphenylhydrazone (Perkin and Stone), 2292.

$C_{21}H_{16}O_2N_2$ Dianilinodialdehydobenzoic acid (Perkin and Stone), 2292.

$C_{21}H_{18}O_2N_4$ Phenylcarbamate of benzeneazobenzylformaldoxime (Walker), 1861.

$C_{21}H_{19}ON$ Benzoyldi-*p*-tolylamine (Chapman), 1998.

N-*p*-Tolylbenzimino-*p*-tolyl ether (Chapman), 1998.

$C_{21}H_{19}O_2N_3$ Benzoin-δ-phenylsemicarbazone (Hopper), 1287.

$C_{21}H_{19}O_4N$ Ethyl diphenacylcyanoacetate (R. M. and J. N. Rây), 2722.

$C_{21}H_{20}O_4N_2$ 2:4-Dihydroxyphenyl *β*-2:4-dihydroxyphenylethyl ketone phenylhydrazone (Chapman and Stephen), 892.

$C_{21}H_{20}O_5N_2$ 1-Cyano-6:7:2′:3′-tetramethoxy-2-benzoyl-1:2-dihydro*iso*quinoline (Haworth and Perkin), 1442.

$C_{21}H_{20}O_9S_3$ Glyceryl tribenzenesulphonate (Fairbourne and Foster), 2762.

$C_{21}H_{21}ON$ *d*-*β*-Amino-αα-diphenyl-*β*-benzylethyl alcohol (McKenzie and Wills), 293.

β-Amino-αα*β*-triphenyl-*β*-methylethyl alcohol (McKenzie and Wills), 292.

$C_{21}H_{22}O_2N_2$ Strychnine, aluminioxalate of (Child, Roberts, and Turner), 2971.

$C_{21}H_{22}O_4N_2$ 1-Cyano-6:7:2′:3′-tetramethoxy-2-benzyl-1:2-dihydro*iso*quinoline (Haworth and Perkin), 1438.

1-Cyano-6:7:3′:4′-tetramethoxy-2-benzyl-1:2-dihydro*iso*quinoline (Haworth, Perkin, and Rankin), 1446.

$C_{21}H_{23}O_5N$ Keto-7-demethylo-ψ-corydaline (Haworth and Perkin), 1461.

$C_{21}H_{23}O_6N$ Ethyl *β*-carboxyanilinobenzylmalonates (Wayne and Cohen), 456.

$C_{21}H_{23}O_7N$ Methyl *N*-homopiperonyl-4:5-dimethoxyhomophthalamate (Haworth, Perkin, and Pink), 1720.

$C_{21}H_{23}O_7Cl$ Delphinidin chloride hexamethyl ether, ($+\frac{1}{2}H_2O$) and its salts (Pratt and Robinson), 174.

$C_{21}H_{24}O_4N_2$ 1-Cyano-6:7:2′:3′-tetramethoxy-2-benzyl-1:2:3:4-tetrahydro*iso*quinoline (Haworth and Perkin), 1441.

1-Cyano-6:7:3′:4′-tetramethoxy-2-benzyl-1:2:3:4-tetrahydro*iso*quinoline (Haworth, Perkin, and Rankin), 1447.

$C_{21}H_{25}O_4N$ 7-Demethylo-ψ-corydaline (Haworth and Perkin), 1460.

Ethyl β-anilino-*p*-tolylmalonate (Wayne and Cohen), 455.

Ethyl β-toluidinobenzylmalonates (Wayne and Cohen), 455.

$C_{21}H_{25}O_5N$ Ethyl β-anilinoanisylmalonate (Wayne and Cohen), 458.

Ethyl β-anisidinobenzylmalonates (Wayne and Cohen), 458.

$C_{21}H_{26}O_4N_2$ Demethylechitamine, and its hydrochloride (Goodson and Henry), 1646.

$C_{21}H_{26}O_5N_2$ 6:7:2′:3′-Tetramethoxy-2-benzyl-1:2:3:4-tetrahydro*iso*quinoline-1-carboxylamide (Haworth and Perkin), 1443.

$C_{21}H_{26}O_6N_2$ 6:7:2′:3′-Tetramethoxy-2-benzyl-1-nitromethyl-1:2:3:4-tetrahydro*iso*quinoline (Haworth and Perkin), 1440.

6:7:3′:4′-Tetramethoxy-2-benzyl-1-nitromethyl-1:2:3:4-tetrahydro*iso*quinoline (Haworth, Perkin, and Rankin), 1447.

$C_{21}H_{27}O_4N$ 6:7:2′:3′-Tetramethoxy-2-benzyl-1-methyl-1:2:3:4-tetrahydro*iso*quinoline, and its picrate (Haworth and Perkin), 1442.

$C_{21}H_{27}O_4N_3$ Ngaione *p*-nitrophenylhydrazone (McDowall), 2203.

$C_{21}H_{31}O_4N$ *O*-Aceto-*N*-undecenovanillylamide (Jones and Pyman), 2598.

$C_{21}H_{44}ON_2$ Eicosylcarbamide (Adam and Dyer), 73.

21 IV

$C_{21}H_{12}N_2Br_2S$ Dibromo-2-α-naphthylamino-β-naphthathiazole (Hunter), 2272.

$C_{21}H_{14}ON_2Cl_2$ 2:2-Dichloro-1:4-*endo*-keto-3:3-diphenyltetrahydroquinoxaline (Ingold and Weaver), 385.

$C_{21}H_{14}N_2Br_4S$ 2-α-Naphthylamino-6-naphthathiazole tetrabromide (Hunter), 2272.

$C_{21}H_{14}N_2Br_6S$ Naphthylaminonaphthathiazole hexabromides (Hunter), 2273.

$C_{21}H_{15}N_2Br_3S$ Naphthylaminonaphthatriazole tribromides (Hunter), 2272.

$C_{21}H_{15}N_2Br_7S$ 2-α-Naphthylamino-β-naphthathiazole heptabromide (Hunter), 2272.

$C_{21}H_{18}O_8N_3As$ 3″-Nitrobenzoyl-3′-amino-4′-anisoyl-4-aminophenylarsinic acid (King and Murch), 2644.

$C_{21}H_{20}O_6N_3As$ 3″-Aminobenzoyl-3′-amino-4′-anisoyl-4-aminophenylarsinic acid, and its salts (King and Murch), 2644.

$C_{21}H_{24}O_4NCl$ Dihydro-7-demethylo-ψ-dehydrocorydalinium chloride (Haworth and Perkin), 1460.

$C_{21}H_{24}O_4NI$ Dihydro-7-demethylo-ψ-dehydrocorydalinium iodide (Haworth and Perkin), 1460.

$C_{21}H_{27}O_{10}N_3S_2$ Dimethoxymethyl*iso*indophenazine dimethosulphate (Armit and Robinson), 1616.

C_{22} Group.

$C_{22}H_{16}O_3$ 7-Hydroxy-3-benzyl-2-phenylbenzo-γ-pyrone (Baker), 2355.

$C_{22}H_{16}O_4$ Dihydroxy-3-benzyl-2-phenylbenzo-γ-pyrones (Baker), 2356.

$C_{22}H_{22}O_7$ 3:4-Dimethoxycinnamic anhydride (Robinson and Shinoda), 1979.

$C_{22}H_{42}O_2$ *n*-Nonadecoylacetone, and its copper salt (Morgan and Holmes), 2896.

$C_{22}H_{44}O_2$ Behenic acid, sodium salt, state of, in solution (Laing), 2751.

22 III

$C_{22}H_{16}O_2N_2$ *o*-Phenoxybenzeneazo-β-naphthol (Turner and Sheppard), 546.

$C_{22}H_{18}ON_2$ 2-*p*-Methoxyphenyl-3-benzylquinoxaline (Malkin and Robinson), 375.

2-Phenyl-3-*p*-methoxybenzylquinoxaline (Malkin and Robinson), 374.

$C_{22}H_{19}O_2N_3$ Benzilmono-δ-benzylsemicarbazone (Hopper), 1286.

$C_{22}H_{20}O_2N_4$ Phenylpyruvic acid oxime phenylcarbamate (Walker), 1862.

$C_{22}H_{21}O_2N_3$ Benzoin-δ-benzylsemicarbazone (Hopper), 1287.

$C_{22}H_{22}O_9N_2$ Anhydrocotarnine-6-nitro-4:5-dimethoxyphthalide (Rây and Robinson), 1621.

$C_{22}H_{23}O_3N$ 3-*p*-Dimethylamino-5-*o*-hydroxystyryl-Δ^5-*cyclo*hexen-1-one (Heilbron, Forster, and Whitworth), 2164.

$C_{22}H_{23}O_6N$ γ-*p*-Dimethylaminocinnamoyl-β-*o*-hydroxyphenylpropane-αα′-dicarboxylic acid (Heilbron, Forster, and Whitworth), 2166.

Dimethyl-2-homopiperonyl-6:7-dimethoxyhomophthalimide (Haworth, Perkin, and Pink), 1720.

$C_{22}H_{24}O_{10}S$ Tetra-acetyl glucoside (Craik and Macbeth), 1639.

$C_{22}H_{28}O_4N_2$ Echitamine, and its salts (Goodson and Henry), 1640.

$C_{22}H_{37}O_2N_3$ Palmitaldehyde-*p*-nitrophenylhydrazone (Stephen), 1876.

22 IV

$C_{22}H_{17}O_2Cl_4Fe$ 7-Methoxy-4-phenylflavylium ferrichloride (Armit and Robinson), 1617.

$C_{22}H_{20}O_9N_3As$ 3″-Nitro-4″-anisoyl-3′-amino-4′-anisoyl-4-aminophenylarsinic acid (King and Murch), 2643.

$C_{22}H_{22}O_7N_3As$ 3″-Amino-4″-anisoyl-3′-amino-4′-anisoyl-4-aminophenylarsinic acid, and its salts (King and Murch), 2643.

$C_{22}H_{28}O_2N_2S_2$ 2:2′-Diacetylethylamino-5:5′-dimethyldiphenyl disulphide (Clark), 974.

$C_{22}H_{28}O_4NCl$ Anhydro-7-demethylomethyl-ψ-corydaline, and its picrate (Haworth and Perkin), 1462.

$C_{22}H_{28}O_4NI$ 7-Demethylo-ψ-corydaline methiodide (Haworth and Perkin), 1460.

C_{23} Group.

$C_{23}H_{16}O_4$ Acetyl derivative of 7-hydroxy-2-phenyl*iso*flavone (Baker and Robinson), 1985.

$C_{23}H_{18}O_{10}$ Datiscetin tetra-acetate (Kalff and Robinson), 1971.

$C_{23}H_{18}O_{11}$ Tetra-acetylquercetin (Kubota and Perkin), 1894.

$C_{23}H_{22}O_{10}$ 3:3′:4′:5′-Tetramethylmyricetin diacetate (Kalff and Robinson), 183.

$C_{23}H_{22}O_{11}$ 2:4:6-Triacetoxy-3′:4′:5′-trimethoxybenzil (Marsh and Stephen), 1637.

$C_{23}H_{44}O_2$ *n*-Eicosanoylacetone, and its copper salt (Morgan and Holmes), 2896.

23 III

$C_{23}H_{15}O_2N$ 7:8-Methylenedioxy-11-phenylindenoquinoline, and its salts (Armit and Robinson), 1610.

$C_{23}H_{17}O_4Cl$ 4′:5:7-Trihydroxy-2-phenyl-4-styrylbenzopyrylium chloride (Walker and Heilbron), 687.

$C_{23}H_{20}O_2N_2$ 2-*p*-Methoxyphenyl-3-*p*-methoxybenzylquinoxaline (Malkin and Robinson), 376.

$C_{23}H_{20}O_3N_2$ Ethyl 3-keto-2:2-diphenyltetrahydroquinoxaline-4-carboxylate (Ingold and Weaver), 384.

Ethyl 4-keto-2:3:3-triphenyldimethylene-1:2-di-imine-1-carboxylate (Ingold and Weaver), 383.

$C_{23}H_{20}O_6S$ 7-Methoxy-4-phenylflavylium methohydroxide (ARMIT and ROBINSON), 1617.

$C_{23}H_{20}BrAs$ Phenylmesitylbenzylmethylarsonium bromide (HUNT and TURNER), 2669.

$C_{23}H_{21}O_3N_3$ Benzophenone-δ-4-carbethoxyphenylsemicarbazone (WILSON and CRAWFORD), 107.

$C_{23}H_{22}O_4N_2$ β-Phenyl-α-carbethoxyhydrazine-β-diphenylacetic acid (INGOLD and WEAVER), 383.

$C_{23}H_{23}O_4N$ 3-*p*-Dimethylaminophenyl-5-*o*-hydroxystyryl-Δ^5-*cyclo*hexen-1-one-2-carboxylic acid (HEILBRON, FORSTER, and WHITWORTH), 2164.

$C_{23}H_{24}O_2N_4$ *dl*-2′-Carboxybenzene-4-azodiphenyl-βγ-diamino-*n*-butanes, and their salts (MORGAN and SKINNER), 1739.

$C_{23}H_{24}O_6N_2$ *p*-Nitrobenzylbenzoyl-*l*-ecgonine, and its salts (GRAY), 1154.

$C_{23}H_{25}O_3N$ 3-(4′-Methoxy-2′-hydroxy)phenyl-5-*p*-dimethylaminostyryl-Δ^5-*cyclo*hexen-1-one (HEILBRON, FORSTER, and WHITWORTH), 2166.

$C_{23}H_{25}O_4N$ Benzylbenzoylecgonines, and their salts (GRAY), 1153, 1158.

$C_{23}H_{25}O_5N$ Benzyl-*o*-hydroxybenzoyl-*l*-ecgonine, and its picrate (GRAY), 1157.

o-Hydroxybenzylbenzoyl-*l*-ecgonine, and its salts (GRAY), 1155.

C_{24} Group.

$C_{24}H_{18}O_3$ 7-Methoxy-2-styryl*iso*flavone (BAKER and ROBINSON), 1986.

$C_{24}H_{18}O_4$ 7-Acetoxy-3-benzyl-2-phenylbenzo-γ-pyrone (BAKER), 2355.

$C_{24}H_{20}O_{11}$ Tetra-acetylquercetin methyl ether (KUBOTA and PERKIN), 1895.

$C_{24}H_{20}Ge$ Tetraphenylgermane (MORGAN and DREW), 1762.

$C_{24}H_{21}N$ Dibenzylquinaldine (MILLS and AKERS), 2477.

$C_{24}H_{22}O$ Benzylidenedibenzylacetone (MILLS and AKERS), 2477.

$C_{24}H_{22}N_2$ Substance, from 1-methyl-2-methylene-1:2-dihydro-β-naphthaquinoline and *p*-dimethylaminobenzaldehyde (MILLS and RAPER), 2472.

$C_{24}H_{42}O_{21}$ Maltodextrin-β (LING and NANJI), 645.

24 III

$C_{24}H_{16}OAs_2$ *oo*′-Diphenylylenearsenious oxide (AESCHLIMANN, LEES, MCCLELAND, and NICKLIN), 69.

$C_{24}H_{17}O_2N$ Anhydro-7:8-methylenedioxy-11-phenylindenoquinoline methohydroxide, and its salts (ARMIT and ROBINSON), 1611.

$C_{24}H_{19}O_4Cl$ 5:7-Dihydroxy-4′-methoxy-2-phenyl-4-styrylbenzopyrylium chloride (WALKER and HEILBRON), 687.

$C_{24}H_{25}O_4N$ Ethyl β-naphthylaminobenzylmalonates (WAYNE and COHEN), 455.

$C_{24}H_{26}O_9S_3$ Glyceryl tri-*p*-toluenesulphonate (FAIRBOURNE and FOSTER), 2762.

$C_{24}H_{27}O_4N$ Phenylethylbenzoylecgonines, and their salts (GRAY), 1155, 1158.

$C_{24}H_{27}O_5N$ Benzylhydroxymethylbenzoyl-*l*-ecgonines, and their picrates (GRAY), 1157.

$C_{24}H_{31}O_3N_3$ Ethyl 3-*p*-dimethylaminophenyl-5-methyl*cyclo*hexan-5-ol-1-one-2-carboxylate phenylhydrazone (HEILBRON, FORSTER, and WHITWORTH), 2165.

$C_{24}H_{41}O_2N_3$ Stearaldehyde *p*-nitrophenylhydrazone (STEPHEN), 1876.

C_{25} Group.

$C_{25}H_{18}O_6$ 7:8-Diacetoxy-2:3-diphenylbenzo-γ-pyrone (BAKER), 2357.

$C_{25}H_{20}O$ Phenyl-α-naphthylmethyl *p*-tolyl ketone (MCKENZIE and TATTERSALL), 2529.

$C_{25}H_{22}O$ αβ-Diphenyl-α(α-naphthyl)-propan-β-ol (MCKENZIE and TATTERSALL), 2527.

$C_{25}H_{24}N_2$ Substance, from 1-ethyl-2-methylene-1:2-dihydro-β-naphthaquinoline and *p*-dimethylaminobenzaldehyde (MILLS and RAPER), 2472.

25 III

$C_{25}H_{19}O_4Cl$ 4′:4″:7-Trihydroxy-2:4-distyrylbenzopyrylium chloride (HEILBRON, WALKER, and BUCK), 694.

$C_{25}H_{21}O_4Cl$ 5:7-Dimethoxy-2′- and -4′-hydroxy-2-phenyl-4-styrylbenzopyrylium chloride (WALKER and HEILBRON), 688.

$C_{25}H_{22}O_4N_2$ Ethyl acetyl-3-keto-2:2-diphenyltetrahydroquinoxaline-4-carboxylate (INGOLD and WEAVER), 384.

$C_{25}H_{24}NI$ Dibenzylquinaldine methiodide (MILLS and AKERS), 2477.

$C_{25}H_{25}N_2I$ Substance, from β-naphthaquinaldine ethiodide and *p*-dimethylaminobenzaldehyde (MILLS and RAPER), 2472.

$C_{25}H_{27}O_4N$ Ethyl 3-*p*-dimethylaminophenyl-5-*o*-hydroxystyryl-Δ^5-*cyclo*hexen-1-one-2-carboxylate (HEILBRON, FORSTER, and WHITWORTH), 2163.

$C_{25}H_{29}O_4N$ Phenyl-*n*-propylbenzoyl-*l*-ecgonine, and its hydrochloride (GRAY), 1156.

$C_{25}H_{29}O_5N$ Benzyltropoyl-*l*-ecgonine, and its salts (GRAY), 1156.

25 IV

$C_{25}H_{22}O_3NCl$ 5:7-Dihydroxy-4′-dimethylamino-2-phenyl-4-styrylbenzopyrylium chloride, and its salts (WALKER and HEILBRON), 687.

C_{26} Group.

$C_{26}H_{20}O_6$ 5:7-Diacetoxy-3-benzyl-2-phenylbenzo-γ-pyrones (BAKER), 2356.

$C_{26}H_{22}N_4$ Benzaldehydediphenylene-4:4′-dihydrazone (CHATTAWAY, IRELAND, and WALKER), 1853.

$C_{26}H_{50}O_6$ Acid, and its salts, from saponification of cutin (LEGG and WHEELER), 1419.

26 III

$C_{26}H_{16}N_4Br_4$ 1:4-Di(2:4-dibromophenyl)-3:6-diphenyl-1:4-dihydro-1:2:4:5-tetrazine (CHATTAWAY and WALKER), 983.

$C_{26}H_{19}O_6Cl$ Trihydroxymethylenedioxy-2:4-distyrylbenzopyrylium chlorides (HEILBRON, WALKER, and BUCK), 696.

$C_{26}H_{20}O_4N_6$ Nitrobenzaldehydediphenylene-4:4′-dihydrazones (CHATTAWAY, IRELAND, and WALKER), 1854.

$C_{26}H_{21}O_4Cl$ Dihydroxymethoxy-2:4-distyrylbenzopyrylium chlorides (HEILBRON, WALKER, and BUCK), 695.

$C_{26}H_{21}O_5Cl$ Trihydroxymethoxy-2:4-distyrylbenzopyrylium chlorides (HEILBRON, WALKER, and BUCK), 695.

$C_{26}H_{23}O_5Cl$ 3′:5:7-Trimethoxy-4′-hydroxy-2-phenyl-4-styrylbenzopyrylium chloride (WALKER and HEILBRON), 689.

$C_{26}H_{24}O_4N_2$ *Py-N*-Methylphenyldiveratro*iso*harmyrine (ARMIT and ROBINSON), 1613.

$C_{26}H_{26}NI$ Dibenzylquinaldine ethiodide (MILLS and RAPER), 2473.

$C_{26}H_{29}O_4N$ Ethyl *p*-dimethylamino-*o*-methoxystyryl-Δ^5-*cyclo*hexen-1-one-2-carboxylates (HEILBRON, FORSTER, and WHITWORTH), 2164.

$C_{26}H_{29}O_5N$ Ethyl 3-*p*-dimethylaminophenyl-5-(methoxy-2′-hydroxy)styryl-Δ^5-*cyclo*hexen-1-one-2-carboxylates (HEILBRON, FORSTER, and WHITWORTH), 2165.

$C_{26}H_{32}O_6N_2$ Diacetylechitamine, hydrochloride of (GOODSON and HENRY), 1645.

$C_{26}H_{32}O_8N_4$ Ethyl 6:6-diphenylhexahydro-1:2:3:4-tetrazine-1:2:3:4-tetracarboxylate (INGOLD and WEAVER), 386.

26 IV

$C_{26}H_{22}O_4N_4As_2$ 3′-Amino-4′-hydroxybenzoyl-4-aminoarsenobenzene (KING and MURCH), 2650.

C_{27} Group.

$C_{27}H_{18}N_2$ 5:6-(2:3-Diphenylindolo) (6:7)-quinoline (Armit and Robinson), 1615.
$C_{27}H_{22}O_{14}$ Myricetin, synthesis of (Kalff and Robinson), 181.
$C_{27}H_{46}O$ Cholesterol, molecular weight of (Partington and Tweedy), 496.

27 III

$C_{27}H_{21}O_6Cl$ 4″:7-Dihydroxy-3″-methoxy-3′:4′-methylenedioxy-2:4-distyrylbenzopyrylium chloride (Heilbron, Walker, and Buck), 696.
$C_{27}H_{23}O_4Cl$ 7-Hydroxy-4′:4″-dimethoxy-2:4-distyrylbenzopyrylium chloride (Heilbron, Walker, and Buck), 694.
$C_{27}H_{26}O_3NCl$ 5:7-Dimethoxy-4′-dimethylamino-2-phenyl-4-styrylbenzopyrylium chloride, and its ferrichloride (Walker and Heilbron), 689.
$C_{27}H_{31}O_4N$ Ethyl 1-methoxy-3-*o*-methoxyphenyl-5-*p*-dimethylaminostyryl-$\Delta^{1:5}$-*cyclo*hexadiene-2-carboxylate (Heilbron, Forster, and Whitworth), 2165.
$C_{27}H_{32}O_3N_2$ Ethyl 3-*p*-dimethylaminophenyl-5-*p*-dimethylaminostyryl-Δ^5-*cyclo*hexen-1-one-2-carboxylate (Heilbron, Forster, and Whitworth), 2165.

C_{28} Group.

$C_{28}H_{18}O$ Dianthranyl oxide (Cooke, Heilbron, and Walker), 2253.
$C_{28}H_{18}S_2$ Dianthranyl disulphide (Cooke, Heilbron, and Walker), 2252.
$C_{28}H_{18}S_4$ Dianthranyl tetrasulphide (Cooke, Heilbron, and Walker), 2254.
$C_{28}H_{20}O$ Phenyl-α-naphthylacetonaphthone (McKenzie and Tattersall), 2529.

28 III

$C_{28}H_{22}O_3N_2$ 2-Keto-3:3:4-triphenyl-1-*p*-nitrobenzyltrimethyleneimine (Ingold and Weaver), 386.
$C_{28}H_{24}O_2N_6$ Benzildi-δ-phenylsemicarbazone (Hopper), 1288.
$C_{28}H_{26}O_2N_4$ Anisaldehydediphenylene-4:4′-dihydrazone (Chattaway, Ireland, and Walker), 1853.
$C_{28}H_{27}O_2N$ *p*-Dimethylaminotetraphenylethylene glycol (Singh), 2446.
$C_{28}H_{27}N_2I$ 6-Methyl-1:1′-diethylcarbocyanine iodide (Mills and Raper), 2474.

28 IV

$C_{28}H_{24}O_2N_2S_2$ 2:2′-Dibenzoylmethylaminodiphenyl disulphide (Clark), 975.
$C_{28}H_{26}O_3NCl$ 7-Hydroxy-4′-methoxy-4″-dimethylamino-2:4-distyrylbenzopyrylium chloride (Heilbron, Walker, and Buck), 695.
$C_{28}H_{28}O_6N_6S_2$ Di-4′-sulphobenzenedis-4-azodiphenyl-βγ-diamino-*n*-butanes, and their salts (Morgan and Skinner), 1735.

C_{29} Group.

$C_{29}H_{28}$ Tetrabenzylmethane (Trotman), 94.

29 II

$C_{29}H_{23}N$ 1-Methyltetraphenylpyrrole (Perkin and Plant), 1141.

29 III

$C_{29}H_{27}N_2Br$ 5:6-Benzo-1:1′-diethylcarbocyanine bromide (Mills and Raper) 2474.

29 IV

$C_{29}H_{28}O_{11}N_4As_2$ 3′-Amino-4′-anisoyl-4-aminophenylarsinic acid *s*-carbamide (King and Murch), 2643.

29 V

$C_{29}H_{43}O_6NBrS$ *d*-4-Phenyl-4′-carbethoxybispiperidinium-1:1′-spiran bromocamphorsulphonates (Mills and Warren), 2512.

C_{30} Group.

$C_{30}H_{20}O_4$ Dimethoxydianthraquinone (PERKIN and YODA), 1887.
$C_{30}H_{44}O_4$ Menthyl benzylidenemalonate (WAYNE and COHEN), 459.

30 III

$C_{30}H_{28}O_2N_6$ Benzildibenzylsemicarbazone (HOPPER), 1286.

30 IV

$C_{30}H_{28}N_4Br_6S_2$ 1-Toluidino-methylbenzthiazole tribromides (HUNTER), 2026.
$C_{30}H_{30}N_4Br_8S_2$ 1-*m*-Toluidino-*m*-toluthiazole tribromide hydrobromide (HUNTER) 2028.

C_{31} Group.

$C_{31}H_{32}ON_2$ Di-*p*-dimethylaminobenzhydryl ketone (SINGH), 2447.

C_{32} Group.

$C_{32}H_{34}$ $\alpha\delta$-Diphenyl-$\beta\gamma$-dibenzyl-$\beta\gamma$-dimethylbutane (TROTMAN), 92.
α-Phenyl-$\beta\beta$-dibenzylpropane (TROTMAN), 93.

32 II

$C_{32}H_{16}O_6$ Diacetoxynaphthadianthrone (PERKIN and YODA), 1886.
$C_{32}H_{20}O_6$ 3:6′-Diacetoxydianthraquinone (PERKIN and YODA), 1886.
$C_{32}H_{22}O_4$ 7-Cinnamoyloxy-2-styryl*iso*flavone (BAKER and ROBINSON), 1986.

32 III

$C_{32}H_{28}O_6N_2$ Anhydro-α-diphenylacetyl-α(or β)-carboxy-β(or α)-carbethoxyhydrazine-β-diphenylacetic acid (INGOLD and WEAVER), 382.

C_{33} Group.

$C_{33}H_{30}O_9$ Rottlerin, preparation of (DUTT), 2046.

C_{34} Group.

$C_{34}H_{30}O_6N_2$ Ethyl 3:5-diketo-4:4:6:6-tetraphenylhexahydropyridazine-1:2-dicarboxylate (INGOLD and WEAVER), 382.

C_{36} Group.

$C_{36}H_{26}N_4$ Cinnamaldehydediphenylene-4:4′-dihydrazone (CHATTAWAY, IRELAND, and WALKER), 1853.
$C_{36}H_{30}Ge_2$ Hexaphenyldigermane (MORGAN and DREW), 1764.
$C_{36}H_{62}O_{31}$ Maltodextrin-α (LING and NANJI), 645.

36 III

$C_{36}H_{30}OGe_2$ Triphenylgermanium oxide (MORGAN and DREW), 1763.
$C_{36}H_{51}O_4N$ Menthyl β-anilinobenzylmalonate (WAYNE and COHEN), 459.

C_{38} Group.

$C_{38}H_{76}O_2$ Dioctadecylacetic acid (ADAM and DYER), 71.

C_{39} Group.

$C_{39}H_{42}O_9$ Methoxyrottlerin (DUTT), 2047.
$C_{39}H_{76}O_4$ Dioctadecylmalonic acid (ADAM and DYER), 71.

C_{41} Group.

$C_{41}H_{40}O_{16}$ Lignol (POWELL and WHITTAKER), 134.
$C_{41}H_{44}O_{10}$ Acetylmethoxyrottlerin (DUTT), 2047.

41 III

$C_{41}H_{44}O_{10}Br_2$ Dibromoacetylmethoxyrottlerin (DUTT), 2047.

C_{44} Group.

$C_{44}H_{24}O_6$ Dibenzoyldihydroxydianthraquinone (PERKIN and YODA), 1887.

C_{47} Group.

$C_{47}H_{44}O_{16}$ Acetylrottlerin (DUTT), 2046.

47 III

$C_{47}H_{44}O_{19}Br_2$ Dibromoacetylrottlerin (DUTT), 2047.

C_{48} Group.

$C_{48}H_{40}O_4Ge_4$ Tetra-anhydrotetrakisdiphenylgermanediol (MORGAN and DREW), 1766.

$C_{48}H_{42}O_5Ge_4$ Trianhydrotetrakisdiphenylgermanediol (MORGAN and DREW), 1766.

C_{51} Group.

$C_{51}H_{57}O_6Al$ Aluminium benzoylcamphor, and its mutarotation (FAULKNER and LOWRY), 1082.

C_{56} Group.

$C_{56}H_{28}Br_2S_2$ *ms*-Dibromodiheptacyclene disulphide (COOKE, HEILBRON, and WALKER), 2254.

C_{75} Group.

$C_{75}H_{84}O_{15}$ Benzoylrottlerin (DUTT), 2047.

ERRATA.

VOL. 115 (1919).

Page	Line	
376	17	*for* "207°" *read* "175°."

VOL. 123 (1923).

2455	13*	*for* "40, 454" *read* "41, 545."
,,	1*	*for* "610" *read* "510."
2456	2	*for* "42, 930" *read* "45, 261."

VOL. 127 (1925).

264	6	*for* "7·5" *read* "7·64."
,,	19	
,,	10	*for* "7·50" *read* "7·64."
,,	21	*for* "0·996" *read* "1·01."
,,	30	

* From bottom.

Vol. 127 (1925).

Page Line

268 17 *for* "(I')" *read* "free iodine (I)"

„ 18 to 34 *replace by* "From the above data we obtain for the composition of the dark equilibrium mixture:

$I' = 0{\cdot}02237$ gm.-ion per litre.

$I_2 = 0{\cdot}00174$ gm.-mol. per litre.

$I_3' = 0{\cdot}00638$ gm.-ion per litre.

Whence we obtain

$$K = \frac{(1{\cdot}625 \times 10^{-2})(0{\cdot}00174)^{\frac{1}{2}}}{(0{\cdot}380 \times 10^{-2})(0{\cdot}02237)} = 7{\cdot}97,$$

a value much lower than those obtained by Maitland or Brönsted."

269 9 *for* "$K = 23{\cdot}6$" *read* "$K = 7{\cdot}97$."

284 11 *for* "CO_2Ph" *read* "CO_2Et."

305 3* *for* "*Low-melting*" read "*High-melting*."

722 Invert Fig. 1.

917 9* atomic number of tungsten, *for* "76" *read* "74."

936 17* *for* "Grafton" *read* "Albemarle."

944 footnote *for* "£75" *read* "£175."

945 1* *for* "based" *read* "placed."

1456 17 for "*ketonor-7-demethylo-ψ-corydaline*" read "*keto-7-demethylo-ψ-corydaline*."

1461 10 *for* "XIII" *read* "XII."

1543 16 & 19 *for* "naphtholbenzoin" *read* "naphtholbenzein."

1745 Formula III. Place "– – –" before "NMe."

1750 7 *for* "(IX)" *read* "(X)."

„ 8 *add* "$CH_2{=}C(CO_2Et)_2$ (X.)"

„ 12 *add* "The correct arrangement is (IX)."

1819 12* *after* "was" *insert* "converted into hydrochlorides and."

1820 6* *before* "of" *insert* "mainly."

2403 Fig. 3 (ordinates) *for* "0, 10, 20, 30, 40" *read* "10, 20, 30, 40, 50."

2435 3 for "*Pyridine*" read "*Nicotine*."

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* From bottom.

3089



ERRATUM.

Vol. 127 (Trans., 1925).

Page	Line	
2997	3*	col. ii *insert* "[with *Frederick J.* **Corby**, *Oliver C.* **Elvins**, *Eveline* **Jones**, *Richard E.* **Kellett**, and *Cyril J. A.* **Taylor**]."

* From bottom.

UNIVERSITY OF ILL... CHEMISTRY

List of Physico-chemical Symbols adopted by the Chemical Society.
[See J.C.S., 1921, **119**, 502—512.]

1. *Mathematical Symbols.*

	Usual symbol.	Alternative symbol.
Base of natural (Napierian) logarithms ...	e	
Diameter	d	
Radius	r	
Ratio of circumference to diameter	π	
Summation.....	Σ	
Variation	δ	
Total differential	d	
Partial differential	∂	

2. *Universal Constants.*

Acceleration due to gravity.....	g	
Mechanical equivalent of heat	J	
Avogadro's constant [number of molecules in 1 gram-molecule (mole)]	N	
Gas constant per mole	R	
Faraday's constant (number of coulombs per gram-equivalent of an ion)	F	
Charge on an electron	e	

3. *General Physics and Chemistry.*

Length	l	
Height.....	h	
Mass	m	
Time	t	
Volume	v, V	
Density (mass per unit volume)	d	D
Pressure	p, P	
Concentration	c, C	
Mole fraction	x	
Critical constants : pressure, volume, temperature (centigrade), temperature (absolute), density	p_c, v_c t_c, T_c d_c	
Reduced quantities : pressure, volume, temperature, density	p_r, v_r t_r, T_r, d	
van der Waals's constants	a, b	
Fluidity	ϕ	
Viscosity	η	
Surface tension	γ	σ
Diffusion coefficient	Δ	
Atomic weight	A	
Molecular weight	M	
Velocity coefficient of reaction	k	
Equilibrium constant	K, (K_c, K_p)	
van't Hoff coefficient	i	
Degree of dissociation (electrolytic, thermal, etc.)	α	

4. *Heat and Thermodynamics.*

	Usual symbol.	Alternative symbol.
Temperature (centigrade)	t	θ
Temperature (absolute)	T	
Critical temperature	t_c, T_c	
Reduced temperature	t_r, T_r	
Critical solution temperature	t_{cs}, T_{cs}	
Quantity of heat	Q	
Entropy	S	
Specific heat	c	
Specific heat at constant pressure	c_p	
Specific heat at constant volume	c_v	
Ratio of specific heats, $c_p : c_v$	γ	
Molecular heat	C	
Molecular heat at constant pressure	C_p	
Molecular heat at constant volume	C_v	
Latent heat per gram	l	
Latent heat per mole	L	
Maximum work (diminution of free energy)	A	

5. *Optics.*

Wave-length of light	λ	
Refractive index	n	n_τ
Specific refractive power (Gladstone and Dale)	r_G, $[r_G]^t_\lambda$	
Specific refractive power (Lorentz and Lorenz)	r_L, $[r_L]^t_\lambda$	
Molecular refractive power	R_G, R_L $[R_G]^t_\lambda$, $[R_L]^t_\lambda$	
Angle of optical rotation	a	
Specific rotatory power	$[a]$	
Molecular rotatory power	$M[a]$	
Specific magnetic rotation	$[\omega]$	
Molecular magnetic rotation	$M[\omega]$	

6. *Electricity and Magnetism.*

Quantity of electricity	Q	
Current intensity	I	
Resistance	R	W
Electromotive force	E	
Electrode potential, or discharge potential of an ion	E	ϵ
Electrode potential referred to the normal hydrogen or normal calomel electrode respectively, the potential of which is taken as zero	E_h, E_c	ϵ_h, ϵ
Normal potential, *i.e.*, the electrode potential referred to the normal hydrogen or normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration	${}_0E_h$, ${}_0E_c$	${}_0\epsilon_h$, ${}_0\epsilon$
Dielectric constant	ϵ	
Conductivity (specific conductance)	κ	
Equivalent conductivity	Λ	
Equivalent conductivity at different dilutions—volumes in litres containing 1 gram-equivalent	Λ_{10}, Λ_v, Λ_∞	

6. *Electricity and Magnetism*—(continued).

	Usual symbol.	Alternative symbol.
Equivalent conductivity of kation and of anion	Λ_k, Λ_a	
Equivalent conductivity of specified ions	Λ_{K^+} $\Lambda_{Cl'}$	
Molecular conductivity	μ	
Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm.	U_k, U_a	
Transport number of kation and of anion	n_k, n_a	
Magnetic permeability	μ	
Magnetic susceptibility	κ	

List of Symbols, Arranged Alphabetically.

Symbol.	Name of quantity.
A	Atomic weight; maximum work.
a	Van der Waals's constant.
b	Van der Waals's constant.
C	Concentration; molecular heat.
c	Concentration; specific heat.
C_p, C_v	Molecular heat at constant pressure, and at constant volume.
c_p, c_v	Specific heat at constant pressure, and at constant volume.
D	Alternative symbol for density.
d	Diameter; total differential; density.
d_c	Critical density.
d	Reduced density.
E	Electromotive force; electrode potential.
e	Base of Napierian logarithms; charge on an electron.
E_h, E_c	Electrode potential referred to the normal hydrogen or the normal calomel electrode, respectively, the potential of which is taken as zero.
${}_0E_h$, ${}_0E_c$	Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration.
F	Faraday's constant (number of coulombs per gram-equivalent of an ion).
g	Acceleration due to gravity.
h	Height.
I	Current.
i	Van't Hoff's coefficient.
J	Mechanical equivalent of heat.
K	Equilibrium constant.
K_c, K_p	Equilibrium constant, when molar concentrations and partial pressures respectively are employed.
k	Velocity coefficient of reaction.
L	Latent heat per mole.
l	Length; latent heat per gram.
M	Molecular weight.
$M[\alpha]$	Molecular rotatory power.
$M[\omega]$	Molecular magnetic rotatory power.
m	Mass.
N	Avogadro's constant (Loschmidt's number) or number of molecules in 1 gram-molecule.
n	Refractive index.

List of Symbols, Arranged Alphabetically—(continued).

Symbol.	Name of quantity.
n_k, n_a	Transport number of kation and of anion.
n_r	Refractive index (alternative symbol).
P	Pressure.
p	Pressure.
p_c, p_r	Critical pressure : reduced pressure.
Q	Quantity of heat; quantity of electricity.
R	Gas constant per mole; electrical resistance.
R_G, R_L	Molecular refractive power, according to Gladstone and Dale, and to Lorentz and Lorenz respectively.
r	Radius.
r_G, r_L	Specific refractive power according to Gladstone and Dale, and to Lorentz and Lorenz respectively.
S	Entropy.
T	Absolute temperature.
T_c	Critical temperature (on the absolute scale).
T_r	Reduced temperature (absolute).
T_{cs}	Critical solution temperature (absolute).
t	Time; temperature (centigrade).
t_c	Critical temperature (centigrade).
t_{cs}	Critical solution temperature (centigrade).
t_r	Reduced temperature (centigrade).
U_k, U_a	Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm.
V	Volume.
v	Volume.
v_c, v_r	Critical volume : reduced volume.
W	Electrical resistance (alternative symbol).
x	Mole fraction.
α	Degree of dissociation (electrolytic, thermal, etc.); angle of optical rotation.
$[\alpha]$	Specific rotatory power.
γ	Surface tension; ratio of specific heats.
Δ	Diffusion coefficient.
δ	Variation.
∂	Partial differential.
ϵ	Electrode potential (alternative symbol); dielectric constant.
ϵ_h, ϵ	Electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, the potential of which is taken as zero (alternative symbols).
${}_0\epsilon_h$, ${}_0\epsilon$	Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration (alternative symbols).
η	Viscosity.
θ	Temperature (centigrade), (alternative symbol).
κ	Specific conductance (conductivity); magnetic susceptibility.
Λ	Equivalent conductivity.
Λ_{10}, Λ_v, Λ_∞	Equivalent conductivity at different dilutions (volumes in litres containing 1 gram-equivalent).
Λ_k, Λ_a	Equivalent conductivity of kation and of anion.
λ	Wave-length of light.
μ	Molecular conductivity; magnetic permeability.
π	Ratio of circumference to diameter.
Σ	Summation.
σ	Surface tension (alternative symbol).
ϕ	Fluidity.
$[\omega]$	Specific magnetic rotation.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, January 15th, 1925, at 8 p.m., Professor W. P. Wynne, D.Sc., F.R.S., President, in the Chair.

The President referred to the loss sustained by the Society, through death, of the following Fellows :

	Elected.	Died.
Robert P. Douglas	May 2nd, 1912.	Nov. 24th, 1924.
Khasberao B. Jadhava	June 16th, 1887.	Oct. 6th, 1924.
Edmund G. Lamb	May 4th, 1893.	Jan. 3rd, 1925.
George Downing Liveing	Nov. 21st, 1853.	Dec. 26th, 1924.
James McAlley	June 15th, 1899.	Feb. 1924.
William Sharman	June 4th, 1874.	Dec. 21st, 1924.

The President announced :

(1) That the names of the Members of Council who retire at the Annual General Meeting on the 26th March, 1925, and who are ineligible for re-election to the same office until the lapse of one year, are as follows :

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President :
Prof. W. P. Wynne.

Foreign Secretary :
Dr. A. W. Crossley.

Vice-Presidents who have filled the office of President :
Prof. H. B. Dixon, Prof. P. F. Frankland.

Vice-Presidents who have not filled the office of President :
Prof. E. C. C. Baly, Dr. J. T. Hewitt.

Ordinary Members of Council :

(*a*) Town Members :
Dr. C. Dorée, Dr. J. J. Fox, Prof. J. R. Partington.

(*b*) Country Members :
Prof. I. M. Heilbron, Prof. J. W. McBain, Dr. W. H. Mills.

The following vacant places fall due to be filled at the Annual General Meeting on March 26th, 1925, in accordance with the Bye-Laws :

President	One vacancy.
Secretaries	One vacancy.
Foreign Secretary	One vacancy.
Vice-Presidents who have filled the office of President	Three vacancies.

(Note : the vacancy additional to the two prescribed by the Bye-Laws is caused by the death of Sir James Dobbie.)

Vice-Presidents who have not filled the office of President	Two vacancies.

Ordinary Members of Council :

(*a*) Town Members (*i.e.*, those living within a radius of 50 miles from Charing Cross)	Five vacancies.
(*b*) Country Members (*i.e.*, those living beyond a radius of 50 miles from Charing Cross)	Two vacancies.

(Note : In accordance with the Bye-Laws, the number of vacancies in each of the categories (*a*) and (*b*) is three. But this year the vacancies among Town Members are increased by two and among Country Members reduced by two, owing to Prof. C. K. Ingold and Prof. J. Reilly, who are no longer resident in the London area, being transferred from Town to Country Members; while the resignation of a Country Member increases the number of vacancies among Country Members from one to two.

The Council has nominated :

Dr. A. W. Crossley to the office of President.
Dr. T. Slater Price to the office of Secretary.
Prof. F. G. Donnan to the office of Foreign Secretary.

(2) That the following address of congratulation was presented by Sir William Pope, F.R.S., to the Société Chimique de France on December 22nd, 1924, on the occasion of the celebrations of the 50th Anniversary of the foundation of Stereochemistry by van't Hoff and Le Bel in 1874 :

" To the Société Chimique de France.

" The President, Council and Fellows of the Chemical Society rejoice to learn that the Société Chimique de France is meeting on December 22nd on the occasion of the 50th anniversary of the foundation of Stereochemistry by Joseph Achille Le Bel and Jacobus Henricus van't Hoff.

"These two savants will ever be remembered for one of the most important advances in modern chemical thought and practice. The masterly conception which they gave to the chemical world has proved a fruitful incentive to brilliant researches, which have not only confirmed their theoretical reasoning, but have also immeasurably widened our knowledge of chemical structure.

"The Chemical Society, which is proud to have the name of Joseph Achille Le Bel on its list of Foreign Fellows, welcomes the opportunity of joining with its sister Society in doing honour to Le Bel and van't Hoff and in paying homage to their genius.

"Signed on behalf of the Chemical Society,

W. P. WYNNE, *President.*

(L.S.)

JOCELYN THORPE, *Treasurer.*

T. SLATER PRICE, } *Secretaries.*
C. S. GIBSON, }

ARTHUR W. CROSSLEY, *Foreign Secretary.*

"Sealed in Council this Eighteenth day of December, One Thousand Nine Hundred and Twenty-four."

The following were formally admitted Fellows of the Chemical Society: H. J. George, E. Rothstein, R. F. Goldstein, S. Barratt, E. Roberts, J. A. Aeschlimann, J. Ross, and C. I. Kelly.

Certificates were read for the first time in favour of:

Claud McClellan Bottomley, B.Sc., 43, Manor Road, Blackburn.
Frederick Stanley Brown, B.Sc., A.I.C., Rosebank, Tile Hill Lane, Coventry.
Herbert Isaac Coombs, B.Sc., B.A., Trinity College, Cambridge.
Ernest James Davis, 45, McClure Street, Ormeon Road, Belfast.
Henry Bell Footner, B.Sc., Great Dean, nr. Christchurch, Hants.
Robert Owen Griffith, M.Sc., A.I.C., Muspratt Laboratory of Physical Chemistry, The University, Liverpool.
Herbert Henry Hodgson, M.A., Ph.D., B.Sc., F.I.C., 136, Paley Road, Bradford.
Wilford Jordayne Johnson, Devanha, South Road, Brighton Beach, Victoria, Australia.
William Wenallt Jones, M.Sc., 19, White Hart Lane, Wood Green, N. 22.
Jacob Kracovski, B.Sc., 11, Ernest Street, E. 1.
John Joseph Laws, 45, Fulham Road, South Kensington, S.W. 7.
Alexander John Simpson Leiper, 74, Whitworth Road, South Norwood, S.E. 25.
William Hamilton McVicker, M.Sc., 45, Wellington Park, Belfast.
Frank Douglas Miles, Caldwell Road, West Kilbride, Ayrshire.
William Bayley Parker, F.I.C., 3, Murray Road, Rugby.
Isaac Vogel, B.Sc., 16, Wellclose Square, E. 1.
Nellie Walker, M.A., Ph.D., B.Sc., 15, Fintry Place, Broughty Ferry.
James Ewart Whipp, 15, St. John's Street, Longsight, Manchester.

The following papers were read:

"6-Chlorophenoxarsine." By E. E. TURNER and A. B. SHEPPARD.

"The chemistry of the three-carbon system. Part III. αβ-βγ-Change in unsaturated acids." By G. A. R. KON and R. P. LINSTEAD.

"The influence of valency direction on the dissociation constants of dibasic acids." By C. H. SPIERS and J. F. THORPE.

"The relation of pilocarpidine to pilocarpine. Synthesis of 1 : 4- and 1 : 5-dimethylglyoxalines." By R. BURTLES, F. L. PYMAN, and J. ROYLANCE.

LECTURE.

Sir William Hardy, Sec.R.S., will deliver his Lecture entitled "Problems presented by Films on Solid Surfaces," on Thursday, February 26th, 1925, at 8 p.m., in the Lecture Hall of the Institution of Mechanical Engineers, Storey's Gate, Westminster, S.W. 1.

ANNIVERSARY DINNER.

The Anniversary Dinner will be held in the Grand Hall of the Hotel Victoria, Northumberland Avenue, W.C. 2, on Thursday, March 26th, 1925, the day of the Annual General Meeting. Further particulars will be issued shortly.

ORDINARY SCIENTIFIC MEETINGS IN FEBRUARY.

February 5th, at 8 p.m.

February 19th, at 8 p.m., when a ballot for the election of Fellows will be held.

List of Papers received between December 19th, 1924, and January 15th, 1925. (This List does not include the titles of papers, or abstracts thereof, which have been read at a Scientific Meeting, or which have appeared in the Journal.)

"Note on a simple constant-level apparatus for thermostats and water-baths." By J. M. SMITH.

"Studies of equilibrium in systems of the type $Al_2(SO_4)_3$–$M''SO_4$–H_2O. Part I. $Al_2(SO_4)_3$–$CuSO_4$–H_2O. $Al_2(SO_4)_3$–$MnSO_4$–H_2O at 30°." By R. M. CAVEN and T. C. MITCHELL.

"The mercuration of aromatic substances. Part I. Toluene." By S. COFFEY.

"The chemistry of the three-carbon system. Part IV. A case of retarded mobility." By G. A. R. KON and R. P. LINSTEAD.

"The velocity of reaction in mixed solvents. Part VIII. The velocity of formation of certain quaternary ammonium salts." By H. McCombie, H. M. Roberts, and H. A. Scarborough.

"Crystalline cuprous bromide." By D. B. Briggs.

"Phenyl benzyl diketone and some derivatives." By T. Malkin and R. Robinson.

"Tautomerism of amidines. Part V. Methylation of glyoxalines by diazomethane. Bromination of 4(or 5)-phenylglyoxaline." By W. G. Forsyth and F. L. Pyman.

"The mass of the hydrogen atom computed." By E. F. Morris.

"The reduction of aromatic nitro-compounds." By R. W. West.

"A redetermination of the atomic weight of boron." By H. V. A. Briscoe and P. L. Robinson.

"The interaction of nitrogen sulphide and sulphur. Nitrogen persulphide." By F. L. Usher.

"The composition of the liquid and vapour phases in mixtures of glycerol and water." By M. P. I. V. Iyer and F. L. Usher.

"Note on some metallic couples decomposing water at the ordinary temperature." By E. S. Hedges and J. E. Myers.

"Styrylbenzopyrylium salts. Part IV. γ-Styryl derivatives of 5 : 7-dihydroxy- and 5 : 7-dimethoxy-2-phenyl-4-methylbenzopyrylium chloride." By G. H. Walker and I. M. Heilbron.

"Styrylbenzopyrylium salts. Part V. Distyryl derivatives of 7-hydroxy-2 : 4-dimethylbenzopyrylium chloride." By I. M. Heilbron, G. H. Walker, and J. S. Buck.

"Interactions of tellurium tetrachloride and acetic anhydride." By G. T. Morgan and H. D. K. Drew.

"Quantitative reduction by hydriodic acid of halogenated malonyl derivatives. Part IV. The influence of substitution in the amide group on the reactivity of the halogen atom in bromomalonamide." By R. W. West.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE BALLOT TO BE HELD AT THE ORDINARY SCIENTIFIC MEETING ON THURSDAY, FEBRUARY 19th, 1925.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

Ashley, Julius Nicholson, 37, Scarsdale Road, Victoria Park, Manchester. British. Chemical Research student at the Victoria University of Manchester. B.Sc. Hons. (Birm.) 1923. A.I.C. 1923. (*Signed by*) Arthur Lapworth, R. Robinson, Frederick Challenger.

Bartram, George Alfred, 19, Valley Rd., Spital, Chesterfield. British. Teacher of Chemistry. Student at University College, Nottingham, 1914–15, 1919 and 1920. B.Sc. (London Pass), 1920; B.Sc. (Lond., 2nd Class Hons. Chem.), 1922. Elected A.I.C. 1923. Teacher of Chemistry 1920 to present time. In charge of Chem. Advanced Course recognised by Board of Education 1922 to present time. (*Signed by*) F. Stanley Kipping, E. B. R. Prideaux, J. B. Firth, A. R. Blackburn.

Beeby, George Harry, 92, Ashby Rd., Loughborough. English. Chemistry Research Student. Training received at Loughborough College, under A. Bramley, Esq., D.Sc., F.I.C., etc. Hold degree of B.Sc. London. 2nd Hons. Chemistry. A.I.C. Diploma of Loughborough College (Hons.). Engaged on Metallurgical Research. (*Signed by*) Arthur Bramley, George Lawton, T. L. Garner, A. T. Eggington.

Bishop, Arthur Henry Burdick, Westminster Training College, 130, Horseferry Rd., Westminster, S.W. 1. British. Assistant Lecturer in Chemistry. Research for one year at Jesus College, Oxford, on "Adsorption of Gases by Glass Wool." At present engaged in research on "Optical Rotatory Dispersion." (*Signed by*) P. C. Austin, E. E. Walker, Gerald Druce.

Bloomer, Vincent, B.Sc., 33, Balfour St., Oldham. British. Student. Have completed 3 years' Honours Chemistry Course at Victoria University, Manchester; am now doing one year's research course for the degree of M.Sc. (*Signed by*) Henry Stephen, F. P. Burt, D. H. Bangham.

Bottomley, Claud McClellan, 43, Manor Road, Blackburn. British. Brewer. B.Sc. (Lond.) [Chemistry taken at Final Exam.]. (*Signed by*) W. J. Stansfield, A. Bramley, G. W. F. Holroyd.

Brown, Frederick Stanley, "Rosebank," Tile Hill Lane, Coventry. British. Research Student (in receipt of a Scientific and Industrial Research Grant). Two years' works experience. Academic training at University College of Wales, Aberystwyth, from 1919 up to present time. 1st Hons. B.Sc. (Wales). A.I.C. Over two years' research experience. *J.C.S.* 1923, Vol. **123**, 2430. *J.C.S.* 1924, Vol. **125**, 2219. (*Signed by*) T. Campbell James, C. R. Bury, Albert Green.

Chorley, Percy, 87, Hazelbottom Rd., Crumpsall, Manchester. British. Chemist. M.Sc. (Vict.). Beyer Fellow, Victoria University, Manchester, 1914. Published, with Professor A. Lapworth, a paper on "A new series of nitrogenous compounds derived from camphoroxalic acid" (*Trans.*, 1920, 728). Chemist, on the staff of British Dyestuffs Corporation, Ltd. (*Signed by*) E. H. Rodd, R. Brightman, H. Swann, Carlton Butler, Morvan Lapworth.

Coombs, Herbert Isaac, Trinity College, Cambridge. British. Student. Bachelor of Science, First-class Bachelor of Arts of Oxford; Research work under Professor Perkin, F.R.S., and Professor Hopkins, F.R.S. (*Signed by*) W. H. Perkin, H. Raymond Ing, R. H. Griffith, N. V. Sidgwick.

Corbet, Alexander Steven, "Abbey Stone House," Sidmouth St., Reading. British. Chemist. B.Sc., Ph.D. (London University). A.I.C. Papers published with Professor H. Bassett: "The Hydrolysis of Potassium Ferricyanide and Potassium Cobalticyanide by Sulphuric Acid," *J.C.S.*, June 1924. "A Phase-rule Study of the Cupro-, Argento-, Auro-, and Thallo-cyanides of Potassium," August, 1924. (*Signed by*) H. Bassett, J. W. Dodgson, D. Roy Maxted.

Crowe, William Haughton, "Bettwsville," Cherry Valley Park, Belfast (N. Ireland). British. Assistant in Chemistry (Q.U.B.). Research in Chemistry, Queen's University, Belfast. 1922–23, subject, "Effect of Light

on Brominations." 1923–24, University College, London, "Pyridones." (*Signed by*) A. W. Stewart, J. K. Marsh, H. Graham.

Davidson, Alfred, 91, Hazelbottom Rd., Cheetham, Manchester. British. Research Chemist, British Dyestuffs Corporation. B.Sc. (Glasgow) with distinction in Chemistry. T. S. Patterson and A. Davidson, *J.C.S.* (1912), **101**, 374. (*Signed by*) E. J. Amies, C. Hollins, S. C. Bate.

Davis, Ernest James, 45, McClure Street, Ormeau Road, Belfast. British. Chief Assistant Chemist, Messrs. Harland and Wolff, Belfast. Ten years Industrial Chemist with Messrs. J. Stone & Co., Deptford; Martin's Heat Treating and Testing Works, Coventry; Harland and Wolff, Ltd., Belfast. (*Signed by*) Henry Wren, Theophilus Harper, James W. Porter.

Duffin, Walter Mark, 35, Binfield Road, S.W. 4. English. Research Student. A.R.C.S. B.Sc., London. Engaged in Research. (*Signed by*) H. B. Baker, G. A. R. Kon, Arnold Stevenson, M. A. Whiteley.

Durrant, Arthur Hynard, 47, Cassiobury Rd., London, E. 17. British. Bacteriologist and Demonstrator in Chemistry, Guy's Hospital and The Technical Institute, E. 17. Inventor of a Constant Cell, see *Junior Mechanic*, May, 1921. (*Signed by*) W. H. Collier, H. L. Long, E. C. Edgar.

Eaton, Frederick John, Ph.D. (Edin.), B.Sc. (Edin.), A.I.C., Chemical Laboratory, Gas Light and Coke Coy., Horseferry Rd., Westminster. British. Research Chemist, Gas Light and Coke Coy. Formerly part time Assistant Dept. of Medical Chemistry, Univ. of Edinburgh, and Research Student under Prof. Barger, F.R.S., Univ. of Edinburgh. Paper on "Blue Adsorption Compounds of Iodine," accepted 9th Sept., 1924. (*Signed by*) George Barger, Ellen Field, John E. Mackenzie.

Edwards, George Alfred, 21, Crystal Palace Rd., London, S.E. 22. British. Demonstrator in Chemistry, King's College, London University. B.A. Oxon., First Class Honours in Chemistry. B.Sc. Oxon. Demonstrator in Chemistry at King's College, London University. Joint author of "Amino-derivatives of Tetrahydrocarbazole." (*Signed by*) Samuel Smiles, A. J. Allmand, E. W. McClelland, Frank W. Stoyle.

Emeléus, Harry Julius, Battle, Sussex. British. Student. Research Student at Imperial College of Science and Technology. Graduate of London University. Chemistry (1st Class Hons.). A.R.C.S. (1st Class Chemistry). (*Signed by*) H. B. Baker, M. A. Whiteley, M. Carlton.

Esdaile, Ralph Margrave, the Lytle Coal Co., Ltd., Minerville, Pa., U.S.A. British. Chemist to the Lytle Coal Co., Ltd., Minerville, Pa., U.S.A. Trained at Finsbury Technical College, 1919–1923. Desires to receive the publications of the Chemical Society. Awarded Diploma, July, 1922, A.C.G.F.C. (*Signed by*) A. J. Hale, H. M. Atkinson, R. J. Seal.

Flack, Edward Hugh St. Clair, 9, Bridge Street, Cambridge. British born subject. Research Student in Organic Chemistry, Univ. of Cambridge. M.Sc. (Univ. of S. Africa). (*Signed by*) W. J. Pope, W. H. Mills, R. C. Odams.

Footner, Henry Bell, Great Dean, nr. Christchurch, Hants. British. Chemist. B.Sc. (Lond.), 1st Hons. Chemistry. 1922–1924, Research work on reactions of Alkyl Thiosulphates and Allied Compounds—publication pending. (*Signed by*) Samuel Smiles, C. Montague Bere, Hubert Painter.

Geoghegan, Desmond, 13, Port View, Heavitree, Exeter. British. Analytical Chemist. Three years pupil-assistant to T. Tickle, Esq., Devon County Analyst; two and a half years' experience in Practical Organic Chemistry and General Chemical Analysis at University College, Exeter, under Prof. W. H. Lewis. Educated at Sherborne School, Dorset, and at Douai School, Berks. Desire Fellowship, to have use of the Library, and

to keep in touch with modern research through the publications of the Society. (*Signed by*) Thomas Tickle, S. Glasstone, F. Southerden, R. King, W. H. Lewis.

Gibby, Clifton William, "The Rise," Foxley Lane, Purley, Surrey. British. Research Worker in Chemistry. Three years' study of Chemistry at University College, London, including a year's research with Professor Irvine Masson. Honours B.Sc. in Chemistry. A.I.C. by Exam. Now appointed Research Assistant to Mr. A. C. Egerton, at the Clarendon Laboratory, Oxford. (*Signed by*) F. G. Donnan, Henry Terrey, L. F. Gilbert.

Gibson, Reginald Oswald, 41, Peak Hill, Sydenham, S.E. 26. British. Research Chemist. Bachelor of Science (London), 1924. Associate of the Institute of Chemistry, 1924. (*Signed by*) F. G. Donnan, W. E. Garner, O. L. Brady, I. E. Weber, V. W. Slater.

Gimingham, Conrad Theodore (F.I.C.), Haddon House, Aarenbury Lane, Harpenden, Herts. British. Research Chemist, Insecticides and Fungicides Dept., Rothamsted Experimental Station, Harpenden, Herts. Research and Advisory Work in Agric. Chemistry at University of Bristol, 1909–1919. Research Work, Chemical Warfare Dept., 1916–1919. Chemist, Research Dept., Olympia Agric. Co., 1920–1923. Since then at Rothamsted Experimental Station. Various papers on Agric. Chem. subjects in *Jour. Agric. Sci.*, *Ann. App. Biol.*, etc. (*Signed by*) E. J. Russell, H. J. Page, H. W. Dudley.

Goodspeed, Jonathan, 36, Vicarage Lane, East Ham, E. 6. Student. Chemistry Student at East London College. (*Signed by*) J. R. Partington, E. E. Turner, B. D. Shaw.

Greenhalgh, Richard, 139, Stuart Street, Clayton, Manchester. British. Research work at Manchester University for M.Sc. Degree. Degree of B.Sc. in Chemistry Honours at Manchester University, Class II, Division I. (*Signed by*) Arthur Lapworth, Henry Stephen, Frederick Challenger, Fred Fairbrother, Colin Campbell.

Griffith, Robert Owen, Muspratt Laboratory of Physical Chemistry, Liverpool University. British. Lecturer in Physical Chemistry, Liverpool University. B.Sc., 1st Class Hons. Chem. (Liverpool), 1914; M.Sc., 1915; A.I.C., 1915–1918. Chemist under D.I.H.E., Liverpool. 1919, Lecturer in Physical Chemistry, Liverpool University. *Publications :* "Einstein's Law of the Photochemical Equivalent," Appendix VII. Lewis's "System of Physical Chemistry," Vol. 3, 3rd edition. Sections "Chemical Equilibrium" and "Reaction Velocity" in "Tables Annuelles de Constanter," Vol. 5 (in print). Papers in *J.C.S.* : (1) 1916, **109**, 67; (2) 1917, **111**, 389; (3) 1921, **119**, 1948; (4) 1923, **123**, 2752; (5) 1923, **123**, 2767. Also *Trans. Faraday Soc.*, 1921, **17**, 525. (*Signed by*) W. C. M. Lewis, F. C. Guthrie, E. C. C. Baly, I. M. Heilbron.

Hailwood, Anthony James, Hazel Bank, Hazel Road, Altrincham. British. Research Chemist in the British Dyestuffs Corporation, Ltd., Manchester. Formerly on the manufacturing staff of the same Corporation. B.Sc. with 1st Class Honours in Physics (Manchester University). *Signed by*) W. H. Perkin, G. R. Clemo, S. C. Bate.

Hiscocks, Edward Stanley, 5, Rosehill, Swansea. British. Research Student, Chemistry Dept., University College, Swansea. Part-time Lecturer in Chemistry to the Municipal Technical College, Swansea. Hons. Graduate (Wales) in Chemistry. Part-time Lecturer in Physical and Inorganic Chemistry to the Municipal Technical College, Swansea. (*Signed by*) J. E. Coates, Leonard E. Hinkel, Ernest E. Ayling.

Hodgson, Herbert Henry, M.A. (Cambridge), B.Sc. (London), Ph.D. (Heidelberg), F.I.C., 136, Paley Road, Bradford. British. Head of Colour Chemistry Dept., Technical College, Huddersfield, since Sept. 1918. Previous posts, 1908–1912, Lecturer and Research Chemist, Technical College, Bradford; 1912–1915, Head of Chemical Dept., Northern Polytechnic Institute, London, N.; 1915–1918, Chief Chemist to Messrs. Brotherton & Co. at Birmingham and Stourton (Leeds). *Papers :* (1) "Dissertation," Heidelberg, 1908; (2) "Some Reactions of Phenyl Iodide, Chloride, and Iodosobenzene Acetate," *Proc. Camb. Phil. Soc.*, 1908; (3) "Isomere organische Magnesiumverbindungen" (with J. Schmidlin), *Ber.*, **41**, 430–437; (4) "Triphenylessigsäure und Tritolylessigsäure" (with J. Schmidlin), *Ber.*, **41**, 438–447; (5) "The Iodination of Phenols, etc." (with W. M. Gardner), *J.C.S.*, 1909, **95**, 1819–1827; (6) "The Development of Sulphuric Acid from Sulphide Dyestuffs and from Free Sulphur" (with W. M. Gardner), *J. Soc. Chem. Ind.*, 1910; (7) "The Action of Sulphur on Amines. Part I. *o*-Toluidine," *J.C.S.*, 1912, **101**, 1693–1701; (8) "The Action of Sulphur on Amines. Part II. Aniline," *J.C.S.*, 1914, **105**, 952–956; (9) "Nitrosation of Phenols. Part I. 3-Chloro-4-nitrosophenol and its Conversion into Two Isomeric Chloroquinone Monoximes" (with F. H. Moore), *J.C.S.*, 1923, **123**, 2499–2507; (10) "The Preparation of 2- and 4-Nitro-1-naphthols" (with E. Kilner), *J.C.S.*, 1924, **125**, 808–811; (11) "Direct Sulphuration of Aniline," *J.C.S.*, 1924, **125**, 1855–1858; (12) "Mononitration of *p*-Chlorotoluene" (with P. Anderson), *J.C.S.*, Oct. Notes, 1924; 4 papers now before the Publication Committee. *Patents :* Some New Sulphur Compounds and Dyestuffs therefrom, 1912; Preparation of Meta Halogenated Phenols, Brit. Pat. 200714; Preparation of Dihalogenated Fluoranes, Brit. Pat. 205254; Preparation of Tautomers of Nitroso-*m*-halogenated Phenols, Brit. Pat. 206734; 2 now filing on *m*-Hydroxybenzaldehyde and Azo Dyestuffs from Alkyl Thiol Amines. (*Signed by*) James Bruce, L. Gordon Paul, R. W. Merriman.

Hughes, David, 18, Holmes Grove, Westbury on Trym, Bristol. British. Chemist. At present on the Staff of British Colloids, Ltd. Passed Qualifying Examination of the Pharmaceutical Society, 1894. Engaged for 10 years in Chemical and Clinical Laboratory Work on my own account in Bath and Clifton. Studied Bacteriology under Prof. Stanley Kent, Bristol University. Co-operated with Dr. A. L. Flemming, Bristol, in a monograph on the Spectroscopic Examination of Blood in Ethyl Chloride Anæsthesia. Desirous of keeping up to date in developments of Chemical Science and to be allowed the privilege of the Library. (*Signed by*) John Macvie Hill, Archibald Macpherson, John F. Ward, Geo. A. Turner.

Hughes, Kathleen Harriet, 8, Ormiston Drive, Knock, Belfast. British. Lecturer in Pure and Applied Chemistry, Municipal College of Technology, Belfast. Lecturer in Chemistry, M.C.T.B., 1920–1924. Temporary Assistant Chemist, Government Laboratory, Strand, 1917–1920. (*Signed by*) Henry Wren, Theophilus Harper, James W. Porter.

Hunt, Arthur Frederick, 6, Seabrooke Cottages, Front Lane, Cranham (nr. Upminster), Essex. Chemical Research Student. B.Sc. (Lond.), 1st Class Hons. Research Student at East London College under Dr. E. E. Turner. (*Signed by*) J. R. Partington, Elwyn Roberts, D. C. Jones, E. E. Turner.

Ingham, Bertram Hobart, Yew Bank, Langham Rd., Bowdon, Cheshire. British. Research Student. B.Sc. Hons., Victoria University, Manchester (*Signed by*) Arthur Lapworth, F. P. Burt, J. E. Myers, Henry Stephen, R. Robinson.

JOHNSON, JOHN DOBNEY, 6, Edward St., Loughborough, Leics. British. Research Student. B.Sc. Hons., London. Royal Scholar. Research Student. (*Signed by*) Jocelyn Thorpe, M. A. Whiteley, G. A. R. Kon, Arnold Stevenson.

JOHNSON, WILFORD JORDAYNE, "Devanha," South Rd., Brighton Beach, Victoria. Licensed Gold Assayer and Chemical Analyst. Associate, Australian Chemical Institute. 1913–1922 (except for War Service), Assistant to Mr. Henry W. Levy, Assayer and Metallurgical Chemist, Melbourne, Australia. September 1922 to date, in partnership with Mr. Henry W. Levy, in private practice as Assayers and Metallurgical Chemists. (*Signed by*) D. O. Shiels, Henry W. Levy, Robert Law.

JONES, CECIL BRELLISFORD OAKES, Old Sewage Works, Whitley, Coventry. British. Analytical Chemist to the Coventry City Council. Four years assistant to W. D. Scouller, Esq., M.Sc., A.I.C., F.C.S. Ten years chief assistant to John Haworth, Esq., F.I.C., F.C.S. Author of "Sewage Works Analyses" (*Surveyor*, April 25th, 1924). (*Signed by*) John Haworth, W. D. Scouller, James H. Kershaw.

JONES, WILLIAM WENALLT, 19, White Hart Lane, Wood Green, N. 22. British. Assist. Chemist, The British Drug Houses, Ltd., Graham St., City Road, N. 1. B.Sc. Wales, June 1922; 2nd Class Honours Chemistry. M.Sc. Wales, June 1924. One session's Research Experience at the University College of North Wales, Bangor. (*Signed by*) Francis H. Carr, Charles Alex. Hill, S. Sugden.

KENNEDY, ALAN RICHMOND, 88, Sellons Avenue, Harlesden, N.W. 10. British. Assistant Chemist (Thomas de la Rue & Co., 110, Bunhill Row, E.C.). Undergraduate (University of London) in Faculty of Science (graduation, 1925). Employed in commercial Laboratory (founded by Dr. Hugo Müller). Desirous of receiving Society's literature concerning particularly modern researches in Organic Chemistry. (*Signed by*) Hubert L. Lucking, P. C. L. Thorne, E. de Barry Barnett, Henry J. S. Sand.

KENYON, FRANK, Power Station, Creekmouth, Barking, Essex. British. Chemist to the New Electrical Station, Barking, County of London Electric Supply Co., Ltd. Associate of the Institute of Chemistry, Branch D. (*Signed by*) J. Kenyon, J. L. White, Harold Hunter.

KING, FREDERICK ERNEST, 101, Cavendish Road, Highams Park, Essex. British. Student (Research at East London College). (*Signed by*) J. R. Partington, E. E. Turner, D. C. Jones.

KNOTT, ERIC, 21, West Richmond St., Edinburgh. British. Lecturer in Chemistry and Physics at the Royal Dispensary and School of Pharmacy of Edinburgh. Student of the Royal Dispensary and School of Pharmacy of Edinburgh, 1919–21, from which place I obtained the Qualifying Certificate of the Pharmaceutical Society and also the Diploma of Pharmaceutical Chemist. For past three years engaged as Lecturer at above School in Chemistry and Physics. (*Signed by*) Russell G. Thin, A. Scott Dodd, William Duncan.

KRACOVSKI, JACOB, 11, Ernest St., London, E. 1. English. Research Student. B.Sc., 1st Class Hons. in Chemistry. At present engaged in research. (*Signed by*) Jocelyn Thorpe, G. A. R. Kon, M. A. Whiteley, E. H. Farmer.

LAMBOURNE, HERBERT, 44, Brighton Road, S. Croydon, Surrey. British. Head of the Chemistry Dept., Borough Polytechnic Institute, Borough Road, S.E. 1. Late Senior Lecturer in Organic Chemistry, University College, Nottingham. Research work on "Quinaldine and Derivatives," "Methyl-

stannonic Acid and Derivatives." M.A. (Cantab.), M.Sc. (Lond.), F.I.C. (*Signed by*) F. S. Kipping, J. B. Firth, E. B. R. Prideaux, F. C. Laxton.

Laws, John Joseph, 45, Fulham Rd., South Kensington. English. Chemist, Dentist, and Optician. Holding the Qualifying Certificate of the Pharmaceutical Society of G.B. (Lond.). Hon. Treasurer of the Chemists' Dental Society of Great Britain and Ireland (Reg. No. 15073). Hon. Gen. Secretary of the Institute of Chemists and Opticians. Examiner in Refraction to the Institute of Chemists and Opticians. Member of the Public Dental Services. At one time principal of the West End College of Chemistry and Pharmacy. Private tutor of Chemistry for many years. (*Signed by*) Percy Barrs, Robert W. Lindsey, James Harry Smith, Frank B. Arnold.

Le Fevre, Raymond James Wood, 17, Broadway Avenue, St. Margarets, Twickenham, Mdx. British. University Undergraduate. Chemistry Student, East London College (2nd year of final). (*Signed by*) J. R. Partington, E. E. Turner, B. D. Shaw.

Leiper, Alexander John Simpson, 74, Whitworth Road, South Norwood, London, S.E. 25. Scottish. Chemist. I wish to join the Chemical Society in order to keep in touch with up-to-date research and proceedings. I am an Associate of the Royal College of Science in Chemistry. (*Signed by*) M. A. Whiteley, Jocelyn Thorpe, James C. Philip.

Lennane, Alfred James Andrew, 22, Ryder St., St. James's, S.W. 1. British. Physician and Surgeon. Formerly Opium Analyst to the Indian Government. M.R.C.S., L.R.C.P. (*Signed by*) Frank Radcliffe, Thos. R. Owles, Samuel Gray Fenton.

Liley, Frederick William, 41, Beaconsfield Rd., West Croydon. British. Assistant, Croydon Borough Analyst. Student at King's College, London. 2 Years assistant to Croydon Borough Analyst. (*Signed by*) Lester Reed, Eric K. Rideal, Ed. Hinks.

Lunt, James Gilbert, 17, York Avenue, Sefton Park, Liverpool. British. B.Sc. of Liverpool. Chemical Analysis, c/o Anglo-South American Meat Co., San Martin 235, Buenos Aires, Argentina. (*Signed by*) I. M. Heilbron, William Doran, Stanley J. C. Snedker.

McVicker, William Hamilton, 45, Wellington Park, Belfast. British. Chemical Research Student. B.Sc. (1st Class Honours), and M.Sc., Queen's University of Belfast. Musgrave Research Student, Queen's University of Belfast, 1923–25. Joint author of 7 papers as follows : *J.C.S.*, **123**, 642, 817, 820, 2147; **125**, 1743; *J. Amer. C. S.*, XLVI, 1351; *Phil. Mag.*, XLVIII, 628. (*Signed by*) A. Killen Macbeth, Ernest W. McClelland, A. W. Stewart, J. K. Marsh, H. Graham.

Mann, Thomas, Alexander Terrace, Bransty, Whitehaven. British. Partner in firm of Hellon and Mann, Analytical and Consulting Chemists, Whitehaven. (*Signed by*) G. W. Martin, C. A. Mitchell, Bernard Dyer.

Mascarenhas, Vincent Mark, Bangalore. Indian Christian. Student, Indian Institute of Science, Bangalore. Bachelor of Arts of the University of Mysore with Chemistry as a main subject. Completed the work on the Chemistry of Indian Black Mustard Seed Oil, and that of Malabar Tallow (*Vateria Indica*) awaiting publication in the Journal of the Indian Institute of Science. (*Signed by*) J. J. Sudborough, M. O. Forster, Roland V. Norris.

Miles, Frank Douglas, Caldwell Road, West Kilbride, Ayrshire. English. Research Chemist. Asst. Lecturer in Inorganic Chemistry, Heriot-Watt College, Edinburgh, 1909–1915. Service in Dept. of Explosives Supply,

1915–1919. Senior Research Chemist, H.M. Factory, Gretna. Chief Research Chemist, Messrs. Burt, Boulton, and Haywood, 1919–1922. At present a member of the Research Section of Nobel Industries, Ltd. *Publications :* "Egyptian Blue," with H. P. Laurie and W. F. P. McLintock, *Proc. Roy. Soc.*, 1914. Also papers in *Proc. Roy. Soc. Edin.* (two, 1915), and in *Journ. Soc. Chem. Ind.*, 1920 and 1922. "A Volumetric Method for the Estimation of Lead," *J.C.S.*, 1915, **107**, 988; "The Solubility of Sulphur Dioxide in Sulphuric Acids" (with J. Fenton), *J.C.S.*, 1920, **117**, 59. Also author of forthcoming volume of Lunge's "Sulphuric Acid and Alkali" entitled, "Sulphuric Acid—Contact Process." (*Signed by*) John Weir, Norman Picton, W. Young.

Nightingale, Edward Arthur, 39, Pacific Rd., Fords Park Rd., Canning Town, E. 16. British. Commercial Analytical Chemist, Messrs. Burt, Boulton, and Heywood, Ltd., Coal Tar and Creosote Works, Silvertown, 1918–1920. Messrs. Pinchin, Johnson & Co., Paint and Varnish Manufacturers, Silvertown, 1920. Student at Borough Polytechnic for Paints, Oils, and Colours. Student at East Ham Technical College, Chemistry, 6 years' course. City and Guilds of London Institute, Coal Tar, 1st Class certificate. (*Signed by*) R. W. Griffiths, W. H. Barker, W. T. Clough.

Offord, Frederick William, 66, Watford Road, Canning Town, London, E. 16. English. Analytical Chemist. National Certificate in Chemistry, "Higher" or "Advanced," 1923. Worked under J. Bendix, F.I.C., F.C.S. (1915–1920). (*Signed by*) E. W. Griffiths, E. G. Churchill, W. H. Barker.

Outridge, Lionel Edward, "Fernhurst," The Avenue, Chingford, Essex. British. Research Student. B.Sc. (London), Honours Chemistry. Research student at East London College under Dr. D. C. Jones. (*Signed by*) J. R. Partington, Elwyn Roberts, D. C. Jones, E. E. Turner.

Parker, Thomas Webster, Mildenhall, Suffolk. British. Chemist. Student at the Royal College of Science (London), 1919–23. A.R.C.S., 1921. Chemist to the Dartmoor China Clay Co. (*Signed by*) James C. Philip, M. B. Donald, A. B. P. Page.

Parker, William Bayley, F.I.C., 3, Murray Road, Rugby, Warwickshire. Chief Chemist (Research and Works), The British Thomson-Houston Co., Ltd., Rugby. Chief Chemist to B.T.H. from April 1902, and Author of "Specifications for Foundry Pig Irons," Pt. I and II., Proceedings British Foundrymens' Association, 1912–13 and 1906; "Specifications for Alloys for High Speed Superheated Steam Turbine Blading," Jnl. Inst. of Metals, No. 2, 1915; "Purchasing Specifications for Resins and Shellac," Jnl. Oil and Colour Chemists' Association, Vol. V, 1922; "Variation of Refractive Index and Density of Benzene with Temperature," W. B. Parker and G. Thompson, *Trans. Chem. Soc.*, 1922, Vol. **121**. (*Signed by*) Percy F. Frankland, S. Judd Lewis, Gartha Thompson.

Parsons, Stuart Russell, 65, Oakfield Road, Ilford. Research Student (Chemistry). B.Sc. (Lond.), Honours Chemistry. A.I.C. Research student at East London College, under Dr. E. E. Turner. (*Signed by*) J. R. Partington, Elwyn Roberts, D. C. Jones, E. E. Turner.

Payne, William Samuel, Moseley House, Rounds Green, Oldbury. English. Chemist. 5 years Laboratory Steward, Oldbury Secondary Schools. 3 years Laboratory Steward, Oldbury Technical Schools. 2 years Demonstrator and Assistant Chemistry Master, Oldbury Technical Schools. U.E.I. Certificate in Advanced Inorganic and Physical Chemistry, 1924. (*Signed by*) John G. Clarke, C. Mansfield Swain, E. Pritchett.

Pierson, Kenneth John, 105, Winterbourne Road, Thornton Heath.

British. Two years Assistant to the Croydon Borough Analyst. (*Signed by*) Lester Reed, Ed. Hinks, Henry P. Stevens.

Pike, Richard Edwin, 6, Haymarket, London, S.W. 1. British. Student. Pass B.Sc. (Lond.). Studying for Honours at Royal College of Science since October, 1923. (*Signed by*) H. B. Baker, H. F. Harwood, M. A. Whiteley, James C. Philip.

Plumbridge, Douglas Victor, 21, Heathfield Rd., Wavertree, Liverpool. British. Research Chemist. Ph.D. (Munich). A.R.C.Sc. (London). A.I.C. On the staff of the Chemical Dept., Messrs. The Salt Union, Ltd., Western Point, Cheshire. (*Signed by*) A. Bramley, Norman M. Comber, James C. Philip.

Preston, John Massey, The Dower House, Euxton, Chorley, Lancs. British. Private Research in Chemistry. B.Sc., 2nd Class Hons. Chem. (Liv.). A.I.C. (*Signed by*) E. C. C. Baly, H. Rogerson, F. C. Guthrie.

Raper, Richard, 12, Mill Lane, Cambridge. British. Research Student. 1st Class Honours in Nat. Sci. Tripos, Parts I and II (Chemistry) of Cambridge University. Two years' research work under Dr. Mills, F.R.S., and two years' experience as Demonstrator in Cambridge University Chemical Laboratory. (*Signed by*) W. J. Pope, W. H. Mills, H. R. Stevens.

Rule, John Frederick James, 29, Alexandra Road, East Ham, E. 6. Research Student. Have passed the B.Sc. Hons. examination in Chemistry of London University, and I am undertaking Research Work under Professor Partington. (*Signed by*) J. R. Partington, W. H. Patterson, E. E. Turner.

Scorah, Leslie Vivian Donald, 139, Dodworth Road, Barnsley (Yorks). British. Research Student. B.Sc. (Hons. Chem.) Sheffield. A.I.C. (*Signed by*) W. P. Wynne, G. M. Bennett, F. G. Tryhorn, Arthur W. Chapman.

Sheppard, George Frederick, 72, Mortlake Rd., Kew Gardens, Surrey. British. Chemist, Cl. II. Department of Government Chemist. Position as above. Student, Royal College of Science, London, 1900–2, passed examinations of the Associateship Course in Chemistry for Revenue Students. Past experience : Analytical work in above Department since November, 1902. (*Signed by*) Thos. J. Cheater, W. Williamson, Robert Robertson, Geo. Stubbs.

Shevlin, Joseph Thomas, "Corwen," Frederick Road, Wylde Green, Birmingham. British. Patent Agent. Associate of the Chartered Institute of Patent Agents. Associate of the Institute of Physics. Associate of the Institution of Electrical Engineers. Fellow Physical Society of London. I am desirous of becoming a Fellow of the Society in order that I may be well versed in the more recent developments in Chemistry. (*Signed by*) G. G. Henderson, F. J. Wilson, E. W. Moss.

Smethurst, Arthur Frederick, Nippon, Cedar Road, Sutton, Surrey. British. Undergraduate. Student in Chemistry at the Royal College of Science since October, 1922. (*Signed by*) H. B. Baker, H. F. Harwood, M. A. Whiteley, James C. Philip.

Smewing, Ethel Minnie, 42, Park Avenue South, Crouch End, N. 8. British. Teacher. B.Sc. Hons. Chem. (Lond.). Teacher of Chemistry. (*Signed by*) J. F. Spencer, M. S. Crewdson, H. Crompton.

Smith, Alton Ewart Clarence, Breydon, Oakmount Avenue, Southampton. British. Lecturer in Physical Chemistry, University College of Southampton. Lecturer as above since 1919. (*Signed by*) D. R. Boyd, C. K. Ingold, C. F. Cross.

Snelus, Suzanne Mabel Lavinia, 67, Elgin Mansions, W. 9. British. Analytical and Consulting Chemist. Member of the Pharmaceutical Society

Associate of the Institute of Chemistry. Senior Analyst to Messrs. Parke Davis & Co. Chemist in Charge to Messrs. J. C. Arnfield & Sons. Assistant Research worker, Dr. F. W. Passmore. (*Signed by*) P. C. L. Thorne, E. de Barry Barnett, Henry J. S. Sand.

Spiers, Claude Hyman, 34, Brondesbury Road, N.W.6. British. Research Chemist. M.A. (Cambridge). B.Sc. (London). Ph.D. (Cambridge). *T.*, 1924, **125**, 450. (*Signed by*) Jocelyn Thorpe, Arnold Stevenson, G. A. R. Kon, H. M. Spiers.

Stern, Harold Jacob, 17, Croxteth Grove, Sefton Park, Liverpool. British. Chemist to firm of paper stainers. Research on Photosynthesis, Liverpool University, 1921–22. Research in Organic Chemistry under Prof. W. H. Perkin, Oxford, 1922–24. B.Sc. (Hons. Chem.), Liv., 1921. Ph.D., Liv., 1923. B.Sc., Oxon., 1924. Baly, Heilbron, and Stern, 1923, **123**, 185. (*Signed by*) W. H. Perkin, Fredk. A. Mason, G. R. Clemo, S. G. P. Plant, E. Hope, F. Raymond Ing.

Still, Charles James, 50, Queen's Parade, Bangor, Co. Down. British. Lecturer in Bleaching and Dyeing, Municipal College of Technology, Belfast. B.Sc. (Lond.); M.Sc. and Ph.D. (Queen's Univ., Belfast). Joint author of several communications (in collaboration with Dr. Henry Wren) on Diphenylsuccinic Acids, published in *J. Chem. Soc*. (*Signed by*) Henry Wren, James W. Porter, Theophilus Harper.

Syed, Mohammad Hassan, Rupar (Amballa), India. Indian Muhammadan. Demonstrator, Maclagan Engineering College, Lahore, India. B.Sc. (Chemistry), Punjab University. Desirous of being in touch with the recent work in Chemistry. (*Signed by*) S. D. Muzaffar, S. J. Kohli, Edwin Theodore Dean.

Thomas, Mary Beatrice, Girton College, Cambridge. Lecturer in Chemistry and Director of Studies in Natural Sciences. Lecturer in Chemistry, Girton College, Cambridge. (*Signed by*) W. J. Pope, F. G. Hopkins, A. Hutchinson.

Timms, Eric Spencer, 96, Grange Park Rd., Thornton Heath. Research Student (Chemistry). B.Sc. (London), Honours Chemistry. Research Student at East London College under Dr. D. C. Jones. (*Signed by*) J. R. Partington, Elwyn Roberts, D. C. Jones, E. E. Turner.

Titterington, Eric, Abdine Palace, Cairo, Egypt. British. Private Chemist to H.M. the King of Egypt. Member of the Pharmaceutical Society of Great Britain. Engaged in the examination of food and all drugs used in the household of His Majesty. Attached to the Medical Staff of His Majesty for Physiological work. Appointed Examiner in Chemistry to the Cairo Medical School, 1924. (*Signed by*) Ayerst Henham Hooker, W. Morris Colles, C. S. Gibson.

Tudhope, Thomas Martin Aitken, 8, Anson Road, Tufnell Park, London, N. 7. British. Temporary Assistant Chemist in the Government Laboratory. B.Sc. (St. Andrews), with Special Distinction in Chemistry. Ph.D. (St. Andrews). Carnegie Research Scholar for two years (sessions 1921–1923). Engaged in Chemical Research at University College, Dundee, for three years. "Optically Active β-Phthalimino-β-phenylpropiophenones," McKenzie and Tudhope, *J.C.S.*, 1924, **125**, 923. (*Signed by*) Robert Robertson, Geo. Stubbs, J. J. Fox.

Vass, Charles Cyril Norrey, "Holmleigh," Harboro' Rd., Kingsthorpe, Northampton. British. Student. B.Sc. Ordinary (Leeds, 1924). (*Signed by*) C. K. Ingold, P. K. Dutt, W. A. Wightman, H. M. Dawson, R. Whytlaw-Gray.

Village, John Harry, 61, Broxholme Lane, Doncaster. British. Chemist. B.Sc. Hons. (Lond.). For 5 years engaged as Assistant Chemist by the Koppers' Coke Oven Co. under G. E. Foxwell, M.Sc., A.Inst.P., F.C.S. Here I have assisted in numerous researches on coal and its by-products. Now in charge of Laboratory. (*Signed by*) G. E. Foxwell, P. G. Mander, G. D. Crosley.

Vogel, Israel, 16, Wellclose Square, London, E. 1. Research Student in Chemistry at the East London College. B.Sc., 1st Class Honours Chemistry. Neil Arnott Scholar and Bronze Medallist in Chemistry of the University of London. Author of "The Constitution of the Thionic Acids," *Chem. News.* **128**, 325–327, 342–345, 361 (1924). (*Signed by*) J. R. Partington, E. E. Turner, D. C. Jones.

Wilson, John, 115, Canterbury Rd., North Harrow. British. Student engaged in Biochemical Research, Imperial College of Science and Technology, M.Sc. (Sheffield). (*Signed by*) S. B. Schryver, Harold Mastin, J. Knaggs.

Walker, Nellie, 15, Fintry Place, Broughty Ferry, Forfarshire. Lecturer in Chemistry, University College, Dundee (University of St. Andrews). M.A., B.Sc., Ph.D. (St. Andrews). Conjoint author of the following papers in the Journal of the Chemical Society: *J.C.S.*, 1914, **105**, 1131; *J.C.S.*, 1915, **107**, 1685; *J.C.S.*, 1922, **121**, 349; *J.C.S.*, 1923, **123**, 2875. (*Signed by*) Alex. McKenzie, J. C. Irvine, John S. W. Boyle.

Ward, William Joseph Victor, 41, Marlowe Rd., Cambridge. English. Research Student. 1st Class Natural Sciences Tripos, Part II, Chemistry 1924, Cambridge. (*Signed by*) W. J. Pope, W. G. Palmer, W. H. Mills.

Whipp, James Ewart, 15, St. John's St., Longsight, Manchester. Pharmacist. Student of the Institute of Chemistry. Fellow of the Biochemical Society. Fellow of the Royal Microscopical Society. Member of the Society of Chemical Industry. (*Signed by*) Henry Garnett, Harry Brindle, Chas. Turner.

Whitehead, Alan Douglas, "Trevorian," 90, West Hill, Putney, S.W. 15. British. Chemist. Student in Dept. of Chemistry, University College, London, Sessions 1921–22, 1922–23, 1923–24. B.Sc. (Lond.), Honours in Chemistry. (*Signed by*) F. G. Donnan, A. Greeves, W. E. Garner.

Williams, Leslie Thomas Douglas, 23, Queen's Gate Gardens, S.W. 7. British. Student. Associateship of the Royal College of Science. I am now performing research at the above college and am desirous of keeping abreast with modern progress in science. (*Signed by*) G. A. R. Kon, M. A. Whiteley, H. L. Riley.

Wylde, John Henry, 203, Boleyn Rd., Forest Gate, E. 7. English. Asst. Chemist, Laboratory of the Gas Light and Coke Coy, Stratford Station. Student at the East Ham Tech. College. National Cert. in Chemistry, Part-time Course, Higher or Advanced (distinction Inorganic Chemistry). City and Guilds of London, Gas Engineering, Ordinary and Honours. (*Signed by*) E. W. Griffiths, W. H. Barker, W. T. Clough.

Yarsley, Victor Emmanuel, The View, Highfield, Chasetown, nr. Walsall. British. Salter Research Fellow, 1924. B.Sc., 1st Hons., School of Chemistry, B'ham. Associate of the Institute of Chemistry. (*Signed by*) G. T. Morgan, H. D. K. Drew, C. E. Wood.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2).

Nair, Sadashiv Parashuram, Nair Building, Lamington Road, Bombay. Indian (British subject). Pharmaceutical Chemist, i/c Powell's Pharma-

ceutical and Chemical Laboratory. Ph.G. (Boston). Graduate of the Massachusetts College of Pharmacy, Boston, Mass. Member of the American Pharmaceutical Association. At present working on finding out the commercial utility of some of the indigenous plants. My aim in joining the Society is to come in contact with the members of the Society and enjoy the privileges given by the same. (*Signed by*) H. B. Tilden.

San, Moung Ba, B.A., 3, Stewart Road, Rangoon, Burma. Burmese. Assistant to the Chemical Examiner to the Government of Burma and Demonstrator in Physics and Chemistry at the Burma Government Medical School, Rangoon. Graduate of Calcutta University (1911–12). Winner of Chemistry Prize (term 1911–12) in the then Govt. College, Rangoon, now the Rangoon University College. No publications yet. 11 years' analytical experience in the Chemical Examiner's Laboratory, comprising examination of Mineral Oils, Drugs, Foodstuffs, Public Water supplies, and also Toxicological and Medico-legal analysis as well as Analysis of Ores, Minerals, and other commodities. (*Signed by*) Thein Kin, William Dallas.

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From the Publishers : Herren Urban & Schwarzenberg.

American Ceramic Society. Bibliography of magnesite refractories. Columbus 1924. pp. 8 + 41. (*Reference.*)

—— Bibliography of silica refractories. Columbus 1924. pp. 125. (*Reference.*) From the Society.

Annales de Chimie. Vols. II., LXIX., LXXXII., LXXXIII. Paris 1789, 1809, 1812. (*For circulation.*) [Incomplete.]

From Professor C. S. Gibson.

Birkbeck College. Centenary Lectures 1823—1923. London 1924. pp. xiv + 178. (*Recd.* 5/1/25.) From Dr. G. Senter.

Brame, John Samuel Strafford. Fuel : solid, liquid and gaseous. 3rd edition. London 1924. pp. xvi + 388. ill. 18*s.* net. (*Recd.* 19/11/24.)

From the Publishers : Messrs. Edward Arnold & Co.

Levy, Stanley Isaac. The rare earths : their occurrence, chemistry and technology. 2nd edition. London 1924. pp. xvi + 362. ill. 18*s.* net. (*Recd.* 19/11/24.)

From the Publishers : Messrs. Edward Arnold & Co.

Niggli, Paul. Lehrbuch der Mineralogie. 2nd edition. I.

Allgemeine Mineralogie. Berlin 1924. pp. xvi + 713. ill. *Gm.* 24. (*Recd.* 18/12/24.)

From the Publishers : Gebrüder Borntraeger.

Physical Society of London, 1874—1924. Proceedings at the Jubilee Celebration Meetings, March 20, 21 and 22, 1924. [London 1924.] pp. vi + 72. ill. (*Reference.*) From the Fleetway Press.

Physics in Industry. Lectures delivered before the Institute of Physics. Vol. II. By Joseph William Mellor, A. E. Oxley, and Cecil Henry Desch. London 1924. pp. 48. ill. 3*s.* net. (*Recd.* 4/12/24.)

From the Publishers : The Oxford University Press.

Revue Générale des Colloïdes et de leurs applications industrielles. Year I, etc. Paris 1923 +. (*Reference.*)

From the Faraday Society.

Schotz, Schachna Peisach. Synthetic organic compounds. London 1925. pp. 412. ill. 45*s.* net. (*Recd.* 19/12/24.)

From the Publishers : Messrs. Ernest Benn.

Sydney Technical College Chemical Society. Journal and Proceedings for 1922. Vol. I. Sydney 1924. pp. 88. ill. (*Reference.*) From the Society.

Thoms, Hermann. [Editor.] Handbuch der praktischen und wissenschaftlichen Pharmazie. Vol. II. Part ii. Vol. III. Part i. Berlin 1924. pp. 288, 288. ill. *Mk.* 20. (*Recd.* 29/12/24.)

From the Publishers : Herren Urban & Schwarzenberg.

Urbain, Georges. L'énergétique des réactions chimiques. Leçons professées a la Sorbonne. Paris [1924]. pp. viii + 268. ill. 25 *fr.* (*Recd.* 24/11/24.)

From the Publisher : M. Gaston Doin.

Waals, Johannes Diderik van der. The continuity of the liquid and gaseous states. (From *Physical Memoirs*, 1890, **1**.) pp. vi + [164]. (*Recd.* 18/12/24.) From Sir Richard Threlfall.

II. *By Purchase.*

Abu 'l-Qāsim Muḥammad. Kitāb al-'ilm al-muktasab fī zirā'at adh-dhahab. Book of knowledge acquired concerning the cultivation of gold. The Arabic text edited with a translation and introduction by Eric John Holmyard Paris 1923. pp. vi + 62 + 54. (*Recd.* 25/10/24.)

Angeli, Angelo. Die Analogien zwischen dem Verhalten einiger Derivate des Benzols und dem der entsprechenden Derivate der aliphatischen Reihe. Translated from the Italian by Fritz Arndt. (Sammlung, Vol. XXVIII.) Stuttgart 1924.

Association of Official Agricultural Chemists. Journal. Vol. VII., etc. Washington 1923 +. (*Reference.*)

Geerligs, Hendrik Coenraad Prinsen. Cane sugar and its manufacture. 2nd edition. London 1924. pp. x + 342. 20*s.* net. (*Recd.* 13/1/25.)

Greaves, Richard Henry, and Wrighton, Harold. Practical microscopical metallography. London 1924. pp. x + 125. ill. 16*s.* net. (*Recd.* 24/11/24.)

Handbuch der Biochemie des Menschen und der Tiere. Edited by Carl Oppenheimer. 2nd edition. Vol. I, etc., Jena 1923 +. (*Recd.* 27/11/24.)

Heyn, E. Die Theorie der Eisen-Kohlenstoff-Legierungen: Studien über das Erstarrungs- und Umwandlungsschaubild, nebst einem Anhang:—Kaltrecken und Glühen nach dem Kaltrecken. Edited by E. Wetzel. Berlin 1924. pp. viii + 186. ill. *Gm.* 12. (*Recd.* 4/12/24.)

Higgins, Sydney Herbert. A history of bleaching. London 1924. pp. viii + 176. ill. 10*s.* 6*d.* net. (*Recd.* 13/1/25.)

Institution of Automobile Engineers. Report of the Empire Motor Fuels Committee: embodying other allied researches. London [1924]. pp. xii + 352. ill. 10*s.* 6*d.* net. (*Recd.* 24/11/24.)

International Rubber Conference. The Rubber Conference, Brussels, 1924: being the Official Report . . . together with the papers read and the discussions thereon. London 1924. pp. 218. ill. 5*s.* net. (*Recd.* 25/11/24.)

Kent-Jones, Douglas William. Modern cereal chemistry. Liverpool 1924. pp. x + 324. ill. 25*s.* net. (*Recd.* 24/11/24.)

Killeffer, D. H. Eminent American chemists: a collection of portraits of eminent Americans in the field of chemistry from the earliest days of the Republic to the present, together with short sketches of the work of each. New York [1924]. pp. v + 33 +33 portraits. (*Reference.*) 30*s.* net.

Kissling, Richard. Chemische Technologie des Erdöls und der ihm nahestehenden Naturerzeugnisse: Erdgas, Erdwachs und Erdpech (Asphalt). 2nd edition. Braunschweig 1924. pp. xviii + 804. ill. *Gm.* 25. (*Recd.* 10/12/24.)

Martin, Louis Claude. Optical measuring instruments: their construction, theory, and use. London 1924. pp. x + 270. ill. 17*s.* 6*d.* net. (*Recd.* 13/1/25.)

[Merck, Emil.] Merck's Reagenzien-Verzeichnis: enthaltend die gebräuchlichen Reagenzien und Reaktionen geordnet nach Autorennamen. 5th edition. [Darmstadt] 1924. pp. vi + 656. (*Reference.*) *Gm.* 18.

Moore, Richard B. [and others]. Analytical methods for

certain metals including cerium, thorium, molybdenum, tungsten, radium, uranium, vanadium, titanium, and zirconium. (Bureau of Mines Bulletin, No. 212.) Washington 1923. pp. xviii + 326. ill. 3*s*. 6*d*. net. (*Recd*. 29/12/24.)

Otto, M. P. L'industrie des parfums d'après de la chimie moderne. Notations et formules. 2nd edition. Paris 1924. pp. xliv + 688. ill. 85 *fr*. (*Recd*. 5/12/24.)

Randell, Wilfrid L. Michael Faraday (1791—1867). London 1924. pp. 192. ill. 4*s*. 6*d*. net. (*Recd*. 24/11/24.)

Ruska, Julius. Arabische Alchemisten. II. Ǵa'far alṢādiq, der sechste Imām. Mit einer Nachbildung der Handschrift Gotha A. 1292 (Haleb 338) in Manuldruck. Heidelberg 1924. pp. 128 + 62. *Gm*. 7.20. (*Recd*. 1/12/24.)

Sherman, Henry Clapp. Food products. 2nd edition. New York 1924. pp. xiv + 688. ill. 14*s*. net. (*Recd*. 25/11/24.)

Treadwell, W. D. Elektroanalytische Methoden. Berlin 1915. pp. x + 233. ill. (*Recd*. 24/11/24.)

United Kingdom. *Permanent Consultative Committee on Official Statistics*. Guide to current official statistics of the United Kingdom. Vol. II (1923): being a systematic survey of official statistics published mainly in 1923, together with an appendix relating to selected statistical publications issued prior to 1923. London 1924. pp. 306. (*Reference*.) 1*s*. net.

Weinland, Rudolf. Einführung in die Chemie der Komplex-Verbindungen (Wernersche Koordinationslehre) in elementarer Darstellung. 2nd edition. Stuttgart 1924. pp. xx + 538. ill. *Gm*. 24. (*Recd*. 24/11/24.)

Zipperer, Paul. Die Schokoladen-Fabrikation: eine Monographie der Kakaofrucht und ihrer Verwertung. 4th edition by Hermann Schaeffer and — Schröder. Berlin 1924. pp. viii + 338. ill. $5 net. (*Recd*. 13/12/24.)

III. *Pamphlets*.

Cohen, Barnett, Gibbs, H. D., and Clark, William Mansfield. Studies on oxidation-reduction. V. Electrode potentials of simple indophenols, each in equilibrium with its reduction product. (From the *U.S. Public Health Reports*, 1924, **39**.)

Evans, Edward Victor. Cantor Lectures on a study of the destructive distillation of coal. London 1924. pp. 49. ill.

Hunter, Harold. The chemical significance of optical dispersion. [London.] 1924. pp. 117. ill.

Robinovitch, Louise G., and Stiles, George W. A chemical basis for the treatment of tuberculosis: experiments on the action

of steapsin and insulin on tubercle bacilli. (From the *Amer. Rev. Tuberculosis*, 1924, **9**.)

Scientific and Industrial Research, Department of. *Food Investigation Board.* Special Report No. 20. The problems of apple transport overseas : a general survey and summary of the results obtained by a scientific expedition to Australia in 1923. By Franklin Kidd and Cyril West. London 1924. pp. vi + 16. ill.

—— *Fuel Research Board.* Technical Paper No. 10. Carbonisation of coal in continuous vertical retorts. A South Wales gas coal. (Mixture of Pentre and No. 3 Rhondda Seams from the Meiros Collieries, Llanharan.) London 1924. pp. iv + 26. ill.

Sinnatt, Frank Sturdy, Simpkin, Neville, and Owles, Archibald Bewick. The inorganic constituents of coal. Part IV. The melting point of coal ash. (*Lancs. & Cheshire Coal Research Assoc.* Bulletin No. 14.) London 1924. pp. 24. ill.

Stern, Arthur Landauer. Contributions to the chemistry of cellulose. I. Cellulose sulphuric acids. London 1894. pp. 28. (Two copies.)

Turner, J. A. Mercurial poisoning : a report on poisoning from small quantities of mercurial vapor. (From the *U.S. Public Health Reports*, 1924, **39**.)

United States. *Department of Agriculture.* Department Bulletin No. 1149. Absorption and retention of hydrocyanic acid by fumigated food products. By Edward L. Griffin [and others.] Washington 1923. pp. 16. ill.

—— —— Department Bulletin No. 1152. Soy and related fermentations. By Margaret B. Church. Washington 1923. pp. 26. ill.

—— —— Department Bulletin No. 1166. Apple by-products as stock foods. By G. P. Walton and George L. Bidwell. Washington 1923. pp. 40. ill.

—— —— Department Bulletin No. 1250. Relation between the composition of California cantaloupes and their commercial maturity. By Edward MacKay Chance, C. G. Church, and F. E. Denny. Washington 1924. pp. 26. ill.

Voegtlin, Carl, Johnson, James McIntosh, and Dyer, Helen. Viscosity and toxicity of arsphenamine solutions. (From the *U.S. Public Health Reports*, 1924. **39**.)

Welch, Marcus Baldwin. Notes on strength of timbers : with list of transverse tests on specimens in the Technological Museum. (*Sydney Technological Museum Bulletin*, No. 6.) Sydney 1923. pp. 12.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, February 5th, 1925, at 8 p.m., Professor W. P. Wynne, D.Sc., F.R.S., President, in the Chair.

The following were formally admitted Fellows of the Chemical Society: E. Lakeman, W. Kilroy, D. McKie, R. F. Barnes, and S. Krishnamurti.

Certificates were read for the first time in favour of:

Niels Janniksen Bjerrum, Vendersgade 28, Copenhagen.
James Herbert Clegg, West Cliffe, Queens Park Road, Burnley.
Horace Cecil Cockroft, B.Sc., A.I.C., 6, Highfield Terrace, Halifax.
Francis Xavier Coyne, 160, Addison Street, Blackburn.
Robin George Westbury Farnell, A.R.C.S., A.I.C., Exeter College, Oxford.
Richard Randolph Garran, B.Sc., Orphir, St. George's Road, Toorak, Melbourne.
James Francis Halpin, F.I.C., 39, Benson Road, Forest Hill, S.E. 23.
John Stanley Heaton, Ph.D., B.Sc., 43, Birch Road, Crumpsall, Manchester.
John Cyril Hensman, M.A., A.I.C., Aldenham School, Elstree.
Horace William Hughes, B.Sc., 27, Ombersley Road, Balsall Heath, Birmingham.
David Bret Jehu, M.Sc., 34, High Street, Welshpool, Montgomeryshire.
Clifford Merton Jones, B.Sc., Buxton Crescent, Newton Hill, Wakefield.
David McDowall, 2, Kennishead Road, Thornliebank, Glasgow.
Richard Alan Morton, B.Sc., Ph.D., A.I.C., 2, Lumley Street, Garston, Liverpool.
Frederick Wilson Moulds, Hill Crest, Villa Road, Nottingham.
David Pomerantz, 15, Nottingham Place, Commercial Road, E. 1.
Robert Joseph Salmon, M.Sc., Holly Bank, Rowton, Chester.
Talrain Singh Prem Chandra Sharma, M.Sc., Engineering College Hostel, Hindu University, Benares, India.
John Robert Shepherd, M.Sc., A.I.C., Lady Hall Farm, Broughton-in Furness.
Leslie John Walker, 45, Devereux Road, Wandsworth Common, S.W. 18.
William Alexander Waters, B.A., 35, Shirley Road, Cardiff.
James Bernard Watson, 30, Mulgrave Road, West Hartlepool.

The following papers were read :

" The chemistry of petroleum. Part I. The occurrence of compounds of sulphur in the light distillate from the crude oil of Maidan-i-Naftun." By S. F. Birch and W. S. G. P. Norris.

" The chemistry of the three-carbon system. Part IV. A case of retarded mobility." By G. A. R. Kon and R. P. Linstead.

" Alternation in the molecular volumes of the normal monobasic fatty acids." By W. E. Garner and E. A. Ryder.

Ordinary Scientific Meeting, Thursday, February 19th, 1925, at 8 p.m., Professor W. P. Wynne, D.Sc., F.R.S., President, in the Chair.

The President referred to the loss sustained by the Society through the death of Dr. Horace T. Brown on February 6th, and announced that the Council had passed the following resolution :

" On behalf of the Chemical Society the Council desires to express its sense of the great loss the Society has sustained in the death of Dr. Horace T. Brown, who served on the Council as Vice-President, Ordinary Member of Council, Treasurer, and Foreign Secretary during a period of twenty years, and offers to his son and daughters deep sympathy in their bereavement."

Certificates were read for the first time in favour of :

Janardhana Ram Bhatt, B.A., Sre Sumangala College, Panadura, Ceylon.
Archibald Beresford Blunsden, The Bungalow, Westbury-on-Trym, Bristol.
Thomas Henry Bowles, Allandale, Meadowside Road, Cheam.
William Harrison Brindley, M.C., M.A., M.Sc.Tech., A.I.C., 11, Millmoor Terrace, Glossop.
Thomas James Elijah Gardner, 12, Bushwood Road, Kew.
Helen Simpson Gilchrist, 82, North Street, St. Andrews.
Frederick Denison Maurice Hocking, M.Sc., A.I.C., 18, Woodside Park Road, N. Finchley, N. 12.
Joseph Taylor Jackson, B.Sc., 192, Algernon Road, Lewisham, S.E. 13.
Ernest Edward Mabbott, B.Sc., 358, Fore Street, Edmonton, N. 9.
Edgar Kent Palmer, B.Sc.Tech., Rose Bank, Victoria Road, Hale, Cheshire.
John Brent Reed, B.Sc., A.I.C., 49, St. Mildred's Road, S.E. 12.
George James Robertson, M.A., B.Sc., Ph.D., The Manse, Stratkinness, St. Andrews.
Leonard William Ernest Townsend, 35, Harewood Road, Collier's Wood, Merton, S.W. 19.
Edwin John Woodcock, Stonecot, Claremont Hill, Jersey.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2) :

James Munsie Bell, Department of Chemistry, University of North Carolina, Chapel Hill, N.C., U.S.A.
John Cameron, Peking Union Medical College, Peking, Chihli, N. China.
Gordon McIntyre, B.Sc., Sarnia, Ontario, Canada.

Dr. B. Flürscheim and Dr. S. Sugden were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared elected as Fellows :

Julius Nicholson Ashley, B.Sc., A.I.C.
George Alfred Bartram, B.Sc., A.I.C.
George Harry Beeby, B.Sc., A.I.C.
Arthur Henry Burdick Bishop.
Vincent Bloomer, B.Sc.
Claude McClellan Bottomley, B.Sc.
Frederick Stanley Brown, B.Sc., A.I.C.
Percy Chorley, M.Sc.
Herbert Isaac Coombs, B.A., B.Sc.
Alexander Steven Corbet, Ph.D., B.Sc., A.I.C.
William Haughton Crowe.
Alfred Davidson, B.Sc.
Ernest James Davis.
Walter Mark Duffin, B.Sc., A.R.C.S.
Arthur Hynard Durrant.
Frederick John Eaton, Ph.D., B.Sc., A.I.C.
George Alfred Edwards, B.A., B.Sc.
Harry Julius Emeléus, B.Sc., A.R.C.S.
Ralph Margrave Esdaile.
Edward Hugh St. Clair Flack, M.Sc.
Henry Bell Footner, B.Sc.
Desmond Geoghegan.
Clifton William Gibby, B.Sc., A.I.C.
Reginald Oswald Gibson, B.Sc., A.I.C.
Conrad Theodore Gimingham, F.I.C.
Jonathan Goodspeed.
Richard Greenhalgh, B.Sc.
Robert Owen Griffith, M.Sc., A.I.C.
Anthony James Hailwood, B.Sc.
Edward Stanley Hiscocks, B.Sc.
Herbert Henry Hodgson, M.A., Ph.D., B.Sc., F.I.C.
David Hughes.
Kathleen Harriet Hughes.
Arthur Frederick Hunt, B.Sc.
Bertram Hobart Ingham, B.Sc.
John Dobney Johnson, B.Sc.
Wilford Jordayne Johnson.
Cecil Brellisford Oakes Jones.
William Wenallt Jones, M.Sc.
Alan Richmond Kennedy.
Frank Kenyon, A.I.C.
Frederick Ernest King.
Eric Knott.
Jacob Kracovski, B.Sc.
Herbert Lambourne, M.A., M.Sc., F.I.C.
John Joseph Laws.
Raymond James Wood Le Fevre.
Alexander John Simpson Leiper, A.R.C.S.
Alfred James Andrew Lennane, M.R.C.S., L.R.C.P.
Frederick William Liley.
James Gilbert Lunt, B.Sc.
William Hamilton McVicker, M.Sc.
Thomas Mann.
Vincent Mark Mascarenhas, B.A.
Frank Douglas Miles.
Sadashiv Parashuram Nair, Ph.G.
Edward Arthur Nightingale.
Frederick William Offord.
Lionel Edward Outridge, B.Sc.
Thomas Webster Parker, A.R.C.S.
William Bayley Parker, F.I.C.
Stuart Russell Parsons, B.Sc., A.I.C.
William Samuel Payne.
Kenneth John Pierson.
Richard Edwin Pike, B.Sc.
Douglas Victor Plumbridge, Ph.D., A.R.C.S., A.I.C.
John Massey Preston, B.Sc., A.I.C.
Richard Raper, B.A.
John Frederick James Rule, B.Sc.
Moung Ba San, B.A.
Leslie Vivian Donald Scorah, B.Sc., A.I.C.
George Frederick Sheppard.
Joseph Thomas Shevlin.
Arthur Frederick Smethurst.
Ethel Minnie Snewing, B.Sc.
Alton Ewart Clarence Smith.
Susanne Mabel Lavinia Snelus, A.I.C.
Claude Hyman Spiers, M.A., Ph.D., B.Sc.
Harold Jacob Stern, Ph.D., B.Sc.
Charles James Still, Ph.D., M.Sc.
Mohammad Hassan Syed, B.Sc.
Mary Beatrice Thomas.
Eric Spencer Timms, B.Sc.
Eric Titterington.
Thomas Martin Aitken Tudhope, Ph.D., B.Sc.

Charles Cyril Norrey Vass, B.Sc.
John Harry Village, B.Sc.
Israel Vogel, B.Sc.
John Wilson, M.Sc.
Nellie Walker, M.A., Ph.D., B.Sc.
William Joseph Victor Ward, B.A.
James Ewart Whipp.
Alan Douglas Whitehead, B.Sc.
Leslie Thomas Douglas Williams, A.R.C.S.
John Henry Wylde.
Victor Emmanuel Yarsley, B.Sc., A.I.C.

The following paper was read :

" The nature of the alternating effect in carbon chains. Part II. The directing influence of the α-methoxyvinyl group in aromatic substitution." By C. K. Ingold and E. H. Ingold.

Dr. T. Slater Price discussed " The action of light on the photographic plate."

ANNUAL GENERAL MEETING.

The Annual General Meeting will take place on Thursday, March 26th, 1925, at 4 p.m., when the President, Professor W. P. Wynne, D.Sc., F.R.S., will deliver his Address.

ANNIVERSARY DINNER.

The Anniversary Dinner will be held in the Grand Hall of the Hotel Victoria, Northumberland Avenue, W.C. 2., on Thursday, March 26th, 1925 (the day of the Annual General Meeting), at 7 for 7.30 p.m. The presence of ladies will be welcomed.

Tickets, price 12*s*. 6*d*. each (including gratuities to waiters) can be obtained from the Assistant Secretary. It will facilitate arrangements if Fellows will apply for tickets at an early date, in any event before March 19th.

List of Papers, or Abstracts thereof, received between January 16th and February 19th, 1925. (This list does not include the titles of papers which have been read at a Scientific Meeting, or which have appeared in the Journal.)

" Colour and molecular geometry. Part III. A graphical presentation of the theory." By J. Moir.

" Tesla-luminescence spectra. Part V. Some polynuclear hydrocarbons." By W. H. McVicker, J. K. Marsh, and A. W. Stewart.

" The surface tensions of aqueous solutions of various organic compounds." By P. R. Edwards.

"The cryoscopic method for adsorption." By H. L. Richardson and P. W. Robertson.

"Ring-chain tautomerism. Part XII. Derivatives of α-ethyl-ββ-dimethylglutaric acid." By G. A. R. Kon, L. F. Smith, and J. F. Thorpe.

"A determination of the melting and transition points of potassium dichromate." By P. L. Robinson, G. E. Stephenson, and H. V. A. Briscoe.

"Interaction of hydrogen and carbon dioxide on the surface of platinum." By C. R. Pritchard and C. N. Hinshelwood.

"The identity of uncineol with eudesmol." By A. R. Penfold.

"Further *X*-ray measurements on long-chain compounds (*n*-hydrocarbons)." By A. Müller and W. B. Saville.

"An *X*-ray investigation of the ketone series." By W. B. Saville and G. Shearer.

"The relationship of thyroxin to tryptophane." By C. S. Hicks.

"A new method of flame analysis." By O. C. de C. Ellis and H. Robinson.

"The movement of flame in closed vessels." By O. C. de C. Ellis and R. V. Wheeler.

"*cyclo*Telluropentanediones containing aliphatic and aromatic substituents." By G. T. Morgan and C. J. A. Taylor.

"3-Chlorobenzopyrylium derivatives." By L. R. Ridgway and R. Robinson.

"A qualitative test for weak bases." By R. Robinson.

"The labile nature of the halogen atom in organic compounds. Part X. The action of hydrazine hydrate on the halogen derivatives of α-nitro-fatty acids." By A. K. Macbeth and D. Traill.

"The effect of colloids on the replacement of lead and copper from their salts by zinc." By L. T. M. Gray.

"A new portable apparatus for the analysis of illuminating and other gases." By H. D. Murray.

"The action of halogen on phenylhydrazones. Part II. The action of chlorine." By J. E. Humphries, H. Humble, and R. Evans.

"Anomalous adsorption." By J. B. Speakman and A. E. Battye.

"The photo-decomposition of chlorine water and of aqueous hypochlorous acid solutions. Part I." By A. J. Allmand, P. W. Cunliffe, and R. E. W. Maddison.

"Studies of dynamic isomerism. Part XVII. The mutarotation of aluminium benzoyl-camphor." By I. J. Faulkner and T. M. Lowry.

"Studies of dynamic isomerism. Part XVIII. The mechanism of mutarotation and of hydrolytic and prototropic change; with a criticism of Baker, Ingold, and Thorpe's doctrine of non-intervention." By T. M. Lowry.

"Studies of dynamic isomerism. Part XIX. Experiments on the arrest of mutarotation in tetramethylglucose." By T. M. Lowry and E. M. Richards.

"The freezing points of hydrofluoric acid." By J. D. C. Anthony and L. J. Hudleston.

"The hydrolysis of iodine as measured by the iodine electrode." By H. D. Murray.

"Some aromatic chlorovinylarsines." By A. F. Hunt and E. E. Turner.

"The mechanism of the reaction between arylhydrazine sulphonic acids and acetoacetic ester." By G. Reeves.

"The compounds formed by the action of bromine upon benzaldehyde-phenylhydrazone." By F. D. Chattaway and A. J. Walker.

"Periodic electrochemical phenomena." By E. S. Hedges and J. E. Myers.

"The nitration of meta-hydroxybenzaldehyde carbonate and ethyl carbonate." By F. A. Mason.

"A synthesis of 1 : 2-dihydroquinaldine." By F. A. Mason.

"The synthesis of 5 : 5′-dibromo-6 : 6′-dimethoxy thioindigo." By R. H. Griffith and E. Hope.

"The interaction of sodium chloride and alumina." By F. H. Clews.

"A resolution of benzoin." By F. J. Wilson and I. V. Hopper.

"Semicarbazones of benzoin. Part I." By I. V. Hopper.

"The 'activation' of graphite as a sorbent of oxygen." By D. H. Bangham and J. Stafford.

"The mechanism of the formation of malachite from basic cupric carbonate." By J. R. I. Hepburn.

"A synthesis of oxyberberine. Part I." By W. H. Perkin, J. N. Rây, and R. Robinson.

"Variation of colour in the fluoresceine family." By J. Moir.

"The equilibria underlying the soap boiling processes. Pure sodium palmitate." By J. W. McBain and G. M. Langdon.

"Some reactions of triethylphosphine." By J. N. Collie.

"Nitro- and amino-ethoxy-lutidine." By J. N. Collie and G. Bishop.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

ADAMKIEWICZ, ALBERT. Die Natur und der Nährwerth des Peptons: eine experimentelle Untersuchung zur Physiologie des Albumins. Berlin 1877. pp. viii + 128. From Dr. H. E. Cox.

ALLEN, ROBERT. Bismuth ores. (Imperial Institute Monograph on Mineral Resources.) London 1925. pp. x + 62. ill. 3*s*. 6*d*. net. (*Recd*. 5/3/25.) From the Director.

ATACK, FREDERICK WILLIAM, assisted by LEONARD WHINYATES. The Chemists' Year Book 1924. American data in collaboration with FRANCIS M. TURNER, Jr. Manchester [1924]. pp. xii + 1164. ill. (*Reference*.) From Mr. L. Eynon.

BÖTTGER, WILHELM. Qualitative Analyse und ihre wissenschaftliche Begründung. 4th—7th edition. Leipzig 1925. pp. xvi + 644 + 34. *M*. 22. (*Recd*. 3/2/25.)
From the Publisher: Herr Wilhelm Engelmann.

CARPENTER, LEONARD. Mechanical mixing machinery. London 1925. pp. 138. ill. 6*s*. net. (*Recd*. 11/2/25.)
From the Publishers: Messrs. Ernest Benn.

CONGRÈS INTERNATIONAL POUR LA RÉPRESSION DES FRAUDES. Compte rendu des travaux du deuxième Congrès, 1909. Paris 1910. pp. viii + 1496. From Dr. H. E. Cox.

DEADLY ADULTERATION and slow poisoning unmasked; or, disease and death in the pot and the bottle. By an enemy to fraud and villany. New edition. London [n. d.]. pp. viii + 190.
From Dr. H. E. Cox.

ELLIOTT, CYRIL. Distillation principles. London 1925. pp. 166. ill. 6*s*. net. (*Recd*. 11/2/25.)
From the Publishers: Messrs. Ernest Benn.

GIBBS, WILLIAM E. The dust hazard in industry. London 1925. pp. 168. ill. 6*s*. net. (*Recd*. 11/2/25.)
From the Publishers: Messrs. Ernest Benn.

GORE, GEORGE, SPARLING, MARCUS, and SCOFFERN, JOHN. Practical chemistry: including the theory and practice of electrodeposition; photographic art; the chemistry of food, with a chapter on its adulterations; and the chemistry of artificial illumination. London 1856. pp. xvi + 574. ill. From Dr. H. E. Cox.

GUYE, CHARLES EUGÈNE. Physico-chemical evolution. Translated by J. R. CLARKE. London 1925. pp. xii + 172. 6*s*. net. (*Recd*. 12/2/25.) From the Publishers: Messrs. Methuen & Co.

HALSE, EDWARD. Antimony ores. (Imperial Institute Monograph on Mineral Resources.) London 1925. pp. x + 102. ill. 5*s*. net. (*Recd*. 5/3/25.) From the Director

HENNINGER, ARTHUR [RODOLPHE MARIE]. De la nature et du role physiologique des peptones. Paris 1878. pp. 68.
From Dr. H. E. Cox.

HOFMANN, FRANZ. Die Bedeutung von Fleischnahrung und Fleischconserven mit Bezug auf Preisverhältnisse. Leipzig 1880. pp. iv + 120. From Dr. H. E. Cox.

JANKE, ALEXANDER. Allgemeine technische Mikrobiologie. I Teil: Die Mikroorganismen. Dresden 1924. pp. xii + 342. ill. *M.* 12. (*Recd.* 3/2/25.) From the Publisher: Herr Theodor Steinkopff.

LOWY, ALEXANDER, and HARROW, BENJAMIN. An introduction to organic chemistry. New York 1924. pp. x + 390. ill. 15*s.* net. (*Recd.* 12/2/25.)
From the London Publishers: Messrs. Chapman & Hall.

PATTERSON, AUSTIN M. A German-English dictionary for chemists. 5th printing, with addenda. New York 1924. pp. xvi + 344. (*Reference.*) 12*s.* 6*d.* net.
From the London Publishers: Messrs. Chapman & Hall.

REVUE GÉNÉRALE DES COLLOÏDES et de leurs applications industrielles. Year I, etc. Paris 1923 +. (*For circulation.*)
From the Biochemical Society.

SEYMOUR, HARTLAND. Agitating, stirring and kneading machinery. London 1925. pp. 140. ill. 6*s.* net. (*Recd.* 11/2/25.) From the Publishers: Messrs. Ernest Benn.

SPIELMANN, PERCY EDWIN. Bituminous substances: scientific progress of practical importance during the last fifteen years. London 1925. pp. xvi + 206. ill. 15*s.* net. (*Recd.* 21/1/25.)
From the Publishers: Messrs. Ernest Benn.

TUNGAY, SYDNEY J. Acid-resisting metals. London 1925. pp. 136. ill. 6*s.* net. (*Recd.* 11/2/25.)
From the Publishers: Messrs. Ernest Benn.

URBAIN, GEORGES. Les notions fondamentales d'élément chimique et d'atome. Paris 1925. pp. iv + 172. 10 *fr.* (*Recd.* 10/2/24.) From the Publishers: MM. Gauthier-Villars et Cie.

WELLINGS, A. W. Chemical symbols, formulæ and calculations. London 1925. pp. viii + 96. 3*s.* net. (*Recd.* 16/1/25.)
From the Publishers: Messrs. Methuen & Co.

II. *By Purchase.*

ARENDT, RUDOLF. Technik der Experimentalchemie: Anleitung zur Ausführung chemischer Experimente. 5th edition. Edited by LUDWIG DOERMER and WALTER FRANCK. Leipzig 1925. pp. xxviii + 732. ill. *M.* 26.50. (*Recd.* 2/2/25.)

FREUNDLICH, HERBERT. The elements of colloidal chemistry. Translated by GEORGE BARGER. London 1925. pp. viii + 210. ill. 7*s.* 6*d.* net. (*Recd.* 19/1/25.)

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Lecture, held in the Lecture Hall of the Institution of Mechanical Engineers, Storey's Gate, Westminster, S.W. 1, on Thursday, February 26th, 1925, at 8 p.m., Professor W. P. WYNNE, D.Sc., F.R.S., President, in the Chair.

Sir WILLIAM HARDY, M.A., Sec.R.S., delivered his Lecture entitled: "Problems presented by Films on Solid Surfaces." A vote of thanks to the Lecturer, proposed by Professor H. E. Armstrong, F.R.S., seconded by Professor A. V. Hill, F.R.S., and supported by the Chairman, was carried with acclamation, and acknowledged by Sir William Hardy.

Ordinary Scientific Meeting, Thursday, March 5th, 1925, at 8 p.m., Professor W. P. WYNNE, D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows:

	Elected.	Died.
Sir Edward Thorpe	Feb. 16th, 1871.	Feb. 23rd.
Alexander Mitchell Williams	Dec. 7th, 1922.	Feb. 21st.

The PRESIDENT also announced that at a Special Meeting of the Council, held on February 26th, 1925, the following resolution was passed:

"On behalf of the Chemical Society, the Council desires to express its profound regret at the death of Sir Edward Thorpe, who for 54 years was a Fellow, and during 39 years served the Society as Member of Council, Vice-President, Treasurer and President, and while Treasurer initiated and supervised the production of the first three volumes of the Collective Indexes of the Society's Journal.

"The Council recognises that by Sir Edward Thorpe's death the

Society loses a wise counsellor and British Chemistry a distinguished investigator, and offers to Lady Thorpe its sincere sympathy in her bereavement."

The Fellows present expressed their concurrence in this resolution by rising from their places.

It was also announced that

(1) With a view to increasing the usefulness of the Library, the Council has made arrangements for the photographic copying by means of the Photostat, of material contained in the Library. Particulars as to cost, etc., can be obtained from the Librarian.

(2) The first lecture in connection with the Fison Memorial Fund, which was established to endow a Lectureship in memory of the late Dr. A. H. Fison, will be delivered by Professor J. J. Thomson, O.M., F.R.S., on Thursday, May 7th, 1925, at 5 p.m., the Right Hon. the Earl of Balfour presiding. The place of meeting will be announced later. Tickets of admission will be obtainable from Mr. S. E. Carr.

The following List of Nominations for vacant places on the Council was read from the Chair :

President : Arthur W. Crossley.

Vice-Presidents who have filled the office of President (3 vacancies) : H. E. Armstrong, A. Scott, W. P. Wynne.

Vice-Presidents who have not filled the office of President (2 vacancies) : J. B. Cohen, N. V. Sidgwick.

Secretary : T. Slater Price.

Foreign Secretary : F. G. Donnan.

Ordinary Members of Council :

(*a*) Town Members, *i.e.*, those resident within 50 miles of Charing Cross (5 vacancies) : H. Bassett, F. W. Gamble, J. Kenyon, B. D. Porritt, G. Stubbs.

(*b*) Country Members, *i.e.*, those resident beyond 50 miles from Charing Cross (2 vacancies) : F. A. Freeth, W. Rintoul, F. J. Wilson.

Dr. P. W. Austin and Dr. E. E. Turner were appointed Scrutators to assist in the counting of votes recorded in the election of the Country Members of Council.

The following were formally admitted Fellows of the Chemical Society : F. H. Banfield, F. Kenyon, A. H. Durrant, A. F. Smethurst, J. D. Johnson, R. E. Pike, C. H. Spiers, S. Dutt, J. Kracovski, H. J. Emeléus, I. Vogel, K. V. Thimann, S. S. G. Sircar, B. T. Narayanan.

The Treasurer drew attention to the fact that on Thursday, March 5th, 1885, exactly 40 years ago, a certificate of a candidate for election as a Fellow was read for the first time in favour of William Palmer Wynne. Commenting on the uniqueness of the occasion, the Treasurer expressed the hope that the President would long be spared to give the Society the benefit of his wise counsel. The meeting showed its hearty approval of the Treasurer's remarks, and the President expressed his sincere thanks for the kind reference.

Certificates were read for the first time in favour of :

Geoffrey Alger Blyde, East Cliffe, East Bank Road, Sheffield.
Frank Henry Charles Bull, B.Sc., A.I.C., 50, Cornwall Road, Bishopston, Bristol.
Harry Dean, 134, New Lane, Oswaldtwistle.
Irvine John Faulkner, Emmanuel College, Cambridge.
Thomas Flett, B.Sc., A.I.C., Anchor Cottage, Kirkwall, Orkney.
John Charles Giblin, B.Sc., A.I.C., 3, Kensington Terrace, Brecon.
Isabel Hodgson Hadfield, M.Sc., 65, Langham Road, Teddington.
Thomas Haworth, 8, Park Terrace, Fielding Lane, Oswaldtwistle.
William Jobson, 52, The Mall, Swindon.
Thomas William Jones, B.Sc., 36, St. Vincent Road, Westcliff-on-Sea.
John Keane, M.Sc., Ph.D., 6 Shamrock Villas, Drumcondra, Dublin.
Andrew Joseph Myles, 12, Gardner Road, Tue Brook, Liverpool.
Alfred William Nash, B.Sc., 18, Prospect Road, Moseley, Birmingham.
Henry Bowen Oakley, M.Sc., A.R.C.S., Wellcome Tropical Research Laboratories, Khartoum.
Harry Rawlings, B.Sc., 15, Station Road, Ramsey, Huntingdon.
Alan Lawrence Smith, M.Sc., 22, Dean Street, Blackpool.
George Thorn, B.Sc., Grove House, Beechen Grove, Watford.
Ernest Swann Watts, Eaglesfield, Limefield Road, Kersal, Manchester.
Archibald Steele Whamond, 22, Church Street, Alloa.
John Stanley Worthington, 27, Rowena Street, Great Lever, Bolton.

The following papers were read :

" Studies of dynamic isomerism. Part XVII. The mutarotation of aluminium benzoylcamphor." By I. J. Faulkner and T. M. Lowry.

" Studies of dynamic isomerism. Part XVIII. The mechanism of mutarotation, and of hydrolytic and prototropic change; with a criticism of Baker, Ingold, and Thorpe's doctrine of non-intervention." By T. M. Lowry.

" Studies of dynamic isomerism. Part XIX. Experiments on the arrest of mutarotation in tetramethylglucose." By T. M. Lowry and E. M. Richards.

Ordinary Scientific Meeting, Thursday, March 19th, 1925, at 8 p.m., Professor W. P. Wynne, D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through the death of Joseph Arderne Ormerod, who was elected a Fellow on May 16th, 1872, and died on March 5th.

R. H. Purcell was formally admitted a Fellow of the Chemical Society.

Certificates were read for the first time in favour of :

James Lindsay Buchan, B.Sc., Hampden Club, N.W. 1.
John Alfred Valentine Butler, M.Sc., The Potteries, Winchcombe, Glos.
Annie Lavinia Byford, B.Sc., 73, Elderton Road, Westcliff-on-Sea.
James Craik, M.A., B.Sc., Ph.D., The University, St. Andrews.
Herbert Greetham Dane, M.Sc., The Diocesan Training College, Winchester.
Margaret Stedman Leonora Dixon, Homebush, Worcester Road, Sutton.
Donald Hanson, 7, Willow Bank, Halifax.
Joseph Hill, 58, Spring Street, Accrington.
Jim Hoyle, 11, Crow Lane, Ramsbottom.
Richard H. F. Manske, M.Sc., The University, Manchester.
Hugh Clonston Moir, B.Sc., A.I.C., 7, Craigielea Street, Dennistoun, Glasgow.
William George Rhodes, 318, Granville Road, Park, Sheffield.
Thomas Kennedy Walker, M.Sc., Ph.D., F.I.C., 4, Swythamley Road, Cheadle Heath, Stockport.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2) in favour of :

Karl Thomas, M.D., The University, Leipzig.
Frederic N. Williams, P.O. Box 1117, Shreveport, La., U.S.A.

The following papers were read :

"The 'activation' of graphite as a sorbent of oxygen." By D. H. BANGHAM and J. STAFFORD.

"Ring-chain tautomerism. Part XIV. The structure of Balbiano's acid." By E. ROTHSTEIN, A. STEVENSON, and J. F. THORPE.

"The tendency towards intramolecular condensation in cyclic keto-esters. Part I. The formation and disruption of bicyclic dihydroresorcinols." By E. H. FARMER and J. ROSS.

"The structure of the enolic forms of β-ketoesters and β-diketones." By N. V. SIDGWICK.

PUBLICATIONS FUND.

In connection with the Appeal for the Publications Fund issued by the Treasurer, it has been decided that a list of donations and subscriptions received shall appear in the Proceedings for June. All donations and subscriptions received prior to the end of May will be included in the List.

LIST OF FELLOWS, 1925.

It has been decided to print the List of Fellows for 1925 and to supply the List to those Fellows who make application to the Assistant Secretary by the 31st July, 1925.

List of Papers, or abstracts thereof, received between February 19th and March 19th, 1925. (This List does not include the titles of papers which have been read at a Scientific Meeting, or which have appeared in the Journal.)

"The isomerism of the oximes. Part XXI. Action of picryl chloride and of 2 : 4-dinitrochlorobenzene on aldoximes." By O. L. Brady and L. Klein.

"Derivatives of semioxamazide. Part III." By F. J. Wilson and E. C. Pickering.

"The stereochemistry of the hydronaphthalenes and related sesquiterpenes. Part I. Decahydro-β-naphthoic acid." By F. W. Kay and N. Stuart.

"Irregularities in the condensation of certain nitriles with resorcinol." By E. Chapman and H. Stephen.

"Studies in the benzothiazole series. Part III. The pseudobases of the *l*-substituted benzothiazole quaternary salts." By L. M. Clark.

"Sulphur compounds removed from a Persian petroleum by means of sulphuric acid. Part I." By E. H. Thierry.

"Ring-chain tautomerism. Part XIII. Three carbon ring-chain tautomerism in a bridged ring system." By J. W. Baker.

"The measurement of the dielectric constants of liquids." By H. Harris.

"Note on the physiological action of certain benzothiazoles and mercaptan derivatives." By R. F. Hunter.

"Note on the physiological action of certain arylamino-derivatives of monochloroacetic acid." By R. F. Hunter.

"The hydrolytic properties of certain amino-acids." By L. P. Bosman.

"The reduction of anethole nitrosochloride." By J. B. Shoesmith and R. H. Slater.

"Investigations on the dependence of rotatory power on chemical constitution. Part XXV. Three optically active alcohols containing a phenyl group and some esters derived therefrom." By L. F. Hewitt and J. Kenyon.

"The integral relations between the vibration frequencies of molecules." By E. C. C. Baly, R. A. Morton, and E. Rogers.

"The photochemical decomposition of nitrosyl chloride." By E. J. Bowen and J. F. Sharp.

"Ray's supposed triethylene trisulphide." By G. M. Bennett and W. A. Berry.

"Hepta- and nono-dilactones." By G. M. Bennett.

"A synthesis of pyrylium salts of anthocyanidin type. Part VI. Polyhydroxyflavylium salts related to chrysin, apigenin, lotoflavin, luteolin, galangin, fisetin, and morin." By D. D. Pratt and R. Robinson.

"Reactions depending upon the vapour at the interface of two immiscible liquids. Part II." By G. Harker and R. K. Newman.

"The hydrates of calcium carbonate." By J. Hume.

"The labile nature of the halogen atom in organic compounds. Part XI. The halogenation of acetylsuccinic ester." By A. K. Macbeth and D. Traill.

"A solid hydride of antimony." By E. J. Weeks and J. G. F. Druce.

"A study of the effect of the concentration of aqueous sodium hydroxide solutions upon the rate of saponification of olive oil." By G. I. Finch and A. Karim.

"The formation of *d*-2 : 2 : 4-trimethyl*cyclo*hexan-3-one-1-carboxylic acid from *d*-camphorquinone." By C. S. Gibson and J. L. Simonsen.

"The reaction between aromatic aldehydes and phenanthraquinone in presence of ammonia." By A. C. Sircar and N. C. G. Ray.

"Studies in heterocyclic compounds. Part I." By A. C. Sircar and P. K. De.

"The action of azides on toluquinone." By F. D. Chattaway and G. D. Parkes.

"The partial pressures of water vapour and of sulphuric acid vapour over concentrated solutions of sulphuric acid at high temperatures." By J. S. Thomas and W. F. Barker.

"Investigations on the dependence of rotatory power on chemical constitution. Part XXVI. Four alcohols containing the vinyl group and some esters derived therefrom." By J. Kenyon and D. R. Snellgrove.

"A synthesis of pyrylium salts of anthocyanidin type. Part VII. The preparation of the anthocyanidins with the aid of triacetylphloroglucinaldehyde." By D. D. Pratt and R. Robinson.

"A synthesis of pyrylium salts of anthocyanidin type. Part VIII. A new synthesis of pelargonidin chloride and of galanginidin chloride." By T. Malkin and R. Robinson.

" The action of halogens upon *m*- and *p*-nitrobenzaldehyde phenylhydrazones." By F. D. Chattaway and A. J. Walker.

" Plant cuticles. Part I. Modern plant cuticles. Studies in the composition of coal." By V. H. Legg and R. V. Wheeler.

" The explosion of ammonia with carbon monoxide and oxygen." By J. W. Beeson and J. R. Partington.

" 3 : 3-Diethylpentane (tetraethylmethane)." By G. T. Morgan, S. R. Carter, and A. E. Duck.

" Aromatic esters of acylecgonines." By W. H. Gray.

" The additive formation of four-membered rings. Part VII. The synthesis and division of some dimethylene-1 : 3-oxaimines." By C. K. Ingold.

" The decomposition of hydrogen peroxide by cobaltic hydroxide." By F. G. Tryhorn and G. Jessop.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Actualités de Chimie Contemporaine. Publiées sous la direction de Albin Haller. 3rd series. Paris 1925. pp. viii + 328. 12 *fr.* net. (*Recd.* 24/2/25.)

From the Publisher : M. Gaston Doin.

Handbuch der Salvarsantherapie. Edited by W. Kolle and K. Zieler. Vol. II. Berlin 1925. pp. xiv + 878. ill. *M.* 34.40. (*Recd.* 16/3/25.) From the Publishers : Messrs. Urban & Schwarzenberg.

II. *By Purchase.*

Gmelins Handbuch der anorganischen Chemie. 8th edition. By Richard Josef Meyer [and others]. Berlin 1924 +. (*Reference.*)

Gnamm, H. Die Gerbstoffe und Gerbmittel. (Chemie in Einzeldarstellungen, Vol. XII.) Stuttgart 1925. pp. xvi + 394. *M.* 24. (*Recd.* 14/3/25.)

Hanslian, Rudolf, and Bergendorff, Fr. Der chemische Krieg : Gasangriff, Gasabwehr und Raucherzeugung. Berlin 1925. pp. iv + 226. ill. *M.* 11. (*Recd.* 10/2/25.)

Holde, David. Kohlenwasserstofföle und Fette sowie der ihnen chemisch und technisch nahestehenden Stoffe. 6th edition. Berlin 1924. pp. xxviii + 856. ill. *M.* 45. (*Recd.* 2/2/25.)

Hoppe-Seyler, Ernst Felix Immanuel. Handbuch der physiologisch- und pathologisch-chemischen Analyse. 9th edition. By Hans Thierfelder. Berlin 1924. pp. xvi + 1004. ill. *M.* 69. (*Recd.* 2/2/25.)

Klöcker, Alb. Die Gärungsorganismen in der Theorie und Praxis der Alkoholgärungsgewerbe. 3rd edition. Berlin 1924. pp. xviii + 448. ill. *Rm.* 12. (*Recd.* 24/2/25.)

Leberle, Hans. Die Bierbrauerei. 2 vols. Stuttgart 1921–25. pp. xii + 307, xii + 589. ill. *M.* 31.80. (*Recd.* 9/3/25.)

Lord, Nathaniel Wright, and Demorest, Dana J. Metallurgical analysis. 5th edition. New York 1924. pp. xxii + 472. ill. 20*s.* net. (*Recd.* 19/1/25.)

Millikan, Robert Andrews. The electron: its isolation and measurement and the determination of some of its properties. 2nd edition. Chicago 1924. pp. xiv + 293. ill. 8*s.* 9*d.* net. (*Recd.* 19/1/25.)

Müller, Erich. Elektrochemisches Praktikum. 4th edition. Dresden 1924. pp. xvi + 264. ill. *M.* 10. (*Recd.* 28/1/25.)

Nernst, Walther. Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes. 2nd edition. Halle (Saale) 1924. pp. viii + 232. ill. *M.* 12. (*Recd.* 10/2/25.)

Ristenpart, Eugen. Chemische Technologie der organischen Farbstoffe. 2nd edition. Leipzig 1925. pp. xiv + 300 + 12 pattern plates. ill. *M.* 15. (*Recd.* 2/2/25.)

Sommerfeld, Arnold. Atombau und Spektrallinien. 4th edition. Braunschweig 1924. pp. xii + 862. ill. *M.* 22. (*Recd.* 28/1/25.)

Strache, Hugo, and Lant, Richard. Kohlenchemie: Entstehung und chemisches Verhalten der Kohlen und ihrer Bestandteile, Untersuchungen der Kohlen. Leipzig 1924. pp. xvi + 600. ill. *M.* 24. (*Recd.* 2/2/25.)

Sutton, Francis. A systematic handbook of volumetric analysis. 11th edition. Revised throughout, with numerous additions, by William Lincolne Sutton and Alfred Edward Johnson. London 1924. pp. x + 630. ill. 35*s.* net. (*Recd.* 19/1/25.)

Taylor, Hugh Stott. [Editor.] A treatise on physical chemistry: a co-operative effort by a group of physical chemists. 2 vols. London 1924. pp. xii + 604 + 42, x + 701 to 1360 + 42. ill. 50*s.* net. (*Recd.* 21/1/25.)

III. *Pamphlets.*

Cohen, Barnett, Gibbs, Harry Drake, and Clark, William Mansfield. Studies on oxidation-reduction. VI. A preliminary study of indophenols: (*a*) dibromo substitution products of phenol indophenol; (*b*) substituted indophenols of the ortho type; (*c*) miscellaneous. (From the *U.S. Public Health Reports*, 1924, **39**.)

Elvove, Elias. A method for the estimation of total sulfur in neoarsphenamine and sulpharsphenamine. (From the *U.S. Public Health Reports*, 1924, **39**.)

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

ANNIVERSARY DINNER.

THE Anniversary Dinner of the Society was held in the Grand Hall, Hotel Victoria, on Thursday, March 26th, 1925, at 7 for 7.30 p.m., Dr. ARTHUR W. CROSSLEY, C.M.G., C.B.E., D.Sc., F.R.S., President, in the Chair. The following is a list of those present :

Aeschlimann, J. A.
Anderson, Rt. Hon. Sir John, G.C.B., *Permanent Under-Secretary of State for Home Affairs.*
Anderson, Miss O. R.
Armstrong, H. E., F.R.S., *Past-President.*
Armstrong, Miss N.
Austin, P. C.
Austin, Mrs. P. C.
Backer, H. J.
Baker, H. B., C.B.E., F.R.S.
Baker, Mrs. H. B.
Baly, E. C. C., C.B.E.
Bassett, H.
Bennett, Miss D. M.
Bennett, J. C. S.
Bennett, G. M.
Bolton, E. R.
Bolton, Mrs. E. R.
Bolton, L. H.
Bolton, Mrs. L. H.
Boyd, D. R.
Brady, O. L.
Brewer, F. M.
Brown, R. B.
Brown, Mrs. R. B.
Burch, W. J. N.
Burgess, W. T.
Burton, H.
Carr, F. H., C.B.E.
Carr, Mrs. F. H.
Carr, Miss M.
Carr, S. E., *Assistant Secretary.*
Chapman, A. Chaston, F.R.S.
Chapman, Mrs. Chaston.
Chapman, A. W.
Chattaway, F. D., F.R.S.
Chemical Age.
Chemistry and Industry.
Clifford, E.
Clifford, F. W., *Librarian.*
Coates, J. E., O.B.E.
Cod, L. M.
Cohen, Ernst, *Nederlandsche Chemische Vereeniging.*
Cohen, Mrs. E.
Collins, S. W.
Cooper, A. J. Bullen.
Cooper, H. Creemer.
Corfield, C. E.
Corfield, Mrs. C. E.
Crossley, A. W., C.M.G., C.B.E., F.R.S., *President.*
Crossley, Mrs. A. W.
Crossley, K. H.
Daily Telegraph.
Dale, H. H., C.B.E., F.R.S.
Desch, C. H., F.R.S.
Dickes, Miss W. E.
Donald, M. B.
Donnan, F. G., C.B.E., F.R.S., *Foreign Secretary.*
Donnan, Miss.

Drew, R. B.
Druce, J. G. F.
Drummond, J. C.
Drummond, Mrs. M. H.
Dudley, H. W., O.B.E.
Dudley, Mrs.
Duncalfe, R.
Dunn, F. P.
Dyer, B.
Dyer, Mrs. B.
Eldridge, A. A.
Eldridge, Mrs. A. A.
Ellingham, H. J. T.
Fargher, R. G.
Fox, J. J., O.B.E.
Freeth, F. A., O.B.E.
Galletly, W. G.
Gardner, J. A.
Garner, W. E.
Gibbons, W. M., O.B.E., *Registrar, Sheffield University.*
Gibson, C. S., O.B.E., *Secretary.*
Gilling, C.
Gordon, J. G.
Gray, J. Hunter, K.C.
Gray, Mrs. J. Hunter.
Gray, W. H.
Greenaway, A. J.
Greeves, A.
Greeves, Mrs. A.
Gregory, Sir Richard.
Griffiths, O. S.
Haas, P.
Hamer, Miss F. M.
Hamer, J. C.
Hamer, Sir William.
Hamer, Lady.
Heath, Sir Frank, K.C.B., *Secretary, Department of Scientific and Industrial Research.*
Henderson, G. G., F.R.S., *President, The Institute of Chemistry.*
Henry, T. A.
Henry, Mrs. T. A.
Hewitt, J. T., F.R.S.
Heycock, C. T., F.R.S.
Hinkel, L. E.
Hinks, E., M.B.E.
Hinks, Mrs. E.
Hoffert, Miss D. A.
Holleman, A. F.
Holleman, Mrs. A. F.
Horton, E.
Hunter, H.
Hutchinson, H. B.
Jackson, Sir Herbert, K.B.E., F.R.S.
Jackson, Lady.
James, T. Campbell.
Jeans, J. H., *Sec. R.S.*
Johnston, T. B., *Dean, Guy's Hospital Medical School.*
Kenyon, J.
King, H.
King, Mrs. H.
Kingston, Miss H. L.
Lakeman, Miss E.
Laker, J.
Lambert, B.
Le Pla, Miss M., *Indexer.*
Lessing, Dr. R.
Lessing, Mrs. R.
Leuchars, W. W., *Prime Warden, The Dyers' Company.*
Levy, Miss E. R.
Lowndes, J.
Lowry, T. M., C.B.E., F.R.S.
McBain, J. W., F.R.S.
McCombie, H., D.S.O., M.C.
Maclean, Mrs. I. S.
Maclean, H.
Macnab, W., C.B.E.
Manning, A. B.
Masson, I., M.B.E.
Meulen, H. ter.
Meulen, Mrs. H. ter.
Miall, S.
Miall, Mrs. S.
Micklethwait, Miss F. M. G., M.B.E.
Mitchell, A. D.
Mitchell, Mrs. A. D.
Monier-Williams, G. W., O.B.E., M.C.
Moody, Mrs. G. T.
Moore, T. S.
Moore, Mrs. T. S.
Morgan, G. T., O.B.E., F.R.S.
Morning Post.
Morrell, G. F.
Morrell, Mrs. G. F.
Morris, H. J.
Mott, B., *President, The Institution of Civil Engineers.*
Newton, A. U.
Neilsen, H.
Neilsen, Mrs. H.
Nuthall, Tallant.
Ormandy, W. R.
Ormandy, Mrs. W. R.

Orton, K. J. P., F.R.S.
Paget, H.
Paget, Mrs. H.
Palmer, W. G.
Palmer, Mrs. W. G.
Pedersen, Kai.
Perkin, W. H., F.R.S., *Past-President.*
Philip, J. C., O.B.E., F.R.S.
Philip, Mrs. J. C.
Pickles, S. S.
Plimmer, R. H. A.
Pope, Sir William J., K.B.E., F.R.S., *Past-President.*
Porritt, B. D.
Pratt, W. R.
Pratt, Mrs. W. R.
Press Association.
Price, T. Slater, O.B.E., F.R.S., *Secretary.*
Price, Mrs. T. Slater.
Pringle, Sir John, C.B.
Pyman, F. L., F.R.S.
Pyman, Mrs. F. L.
Raven, Sir Vincent, K.B.E., *President, The Institution of Mechanical Engineers.*
Reid, R. B., *President, The Institute of Brewing.*
Roberts, E.
Robertson, Mrs. E. G.
Robertson, Sir Robert, K.B.E., F.R.S.
Robertson, Lady.
Rogers, H.
Rosedale, J. L.
Rowlands, M. J.
Russell, A. S.
Sargeant, F. Pilkington, *President, The Pharmaceutical Society.*
Scott, A., F.R.S., *Past-President.*
Scott, Mrs. A.
Sharp, T. M.
Sharp, Mrs. T. M.
Sidgwick, N. V., F.R.S.
Simonsen, J. L.
Simonsen, Mrs. J. L.
Simpson, G. C., C.B.E., F.R.S.
Simpson, Mrs. G. C.
Smith, C., *Editor.*
Smith, Miss M. L.
Smith, T. B.
Spielmann, P. E.
Stern, A. L.
Stern, Mrs. A. L.
Stubbs, G., C.B.E.
Stubbs, Mrs. G.
Sugden, S.
Taylor, Miss M.
Thomas, R. N. Garrod.
Thomson, J. Millar, F.R.S.
Thorpe, J. F., C.B.E., F.R.S., *Treasurer.*
Thorpe, Mrs. J. F.
Times.
Tinkler, C. K.
Tinkler, Mrs. C. K.
Tryhorn, F. G.
Tryhorn, Mrs. F. G.
Turner, E. E.
Turner, Miss E. G.
Turner, G. W.
Turner, T., *President, The Institute of Metals.*
Voelcker, E.
Voelcker, E. W.
Voelcker, J. A.
Whiteley, Miss M. A., O.B.E.
Widdows, Miss S. T.
Woolcock, W. J. U., C.B.E., *President, The Society of Chemical Industry.*
Wynne, Miss D. P.
Wynne, W. P., F.R.S., *Past-President.*

After the loyal toasts had been honoured the President announced that he had had a telegram from Professors Biilmann, Bjerrum, Bohr, Brönsted, and Sörensen sending their hearty greetings and congratulations to the Society. This was received with acclamation.

The following is a list of the Toasts proposed :—

1. " His Most Gracious Majesty The King."

2. " Their Majesties the Queen and Queen Alexandra, His Royal Highness the Prince of Wales, and the other members of the Royal Family."

*

By Sir H. Frank Heath, K.C.B., Secretary of the Department of Scientific and Industrial Research :—

3. "The Chemical Society," coupled with the name of the President.

By Professor Henry E. Armstrong, LL.D., F.R.S., Past-President :—

4. "The Retiring President, Professor W. P. Wynne, D.Sc., F.R.S."

By Professor Irvine Masson, M.B.E., D.Sc. :—

5. "The Federated Societies," coupled with the name of W. J. U. Woolcock, Esq., C.B.E., President of the Society of Chemical Industry.

By Professor F. G. Donnan, C.B.E., D.Sc., F.R.S., Foreign Secretary :—

6. "The Guests," coupled with the names of Professor Ernst Cohen, of Utrecht University (representing the Nederlandsche Chemische Vereeniging), and J. Hunter Gray, Esq., K.C., M.A.

Sir H. Frank Heath, K.C.B., in proposing the toast of "The Chemical Society," said :—

Mr. President, Ladies and Gentlemen, after I had accepted with some hesitation the invitation to address you this evening, and to propose this toast, I happened to be present at a public dinner where one of His Majesty's Judges said that after considerable experience of speeches of the kind he had come to the conclusion that most proposers of toasts began by explaining how unfitted they were for the task entrusted to them, and spent the rest of the time in proving it. Well, Ladies and Gentlemen, after that opinion from the Bench, there is nothing left for me but to throw myself on the mercy of the court.

I do, indeed, feel it to be a very great honour that a great scientific society like this should ask to have the principal toast of the evening proposed by a layman. You are not only a focus of research in pure science, you not only have a membership of 4,000 Fellows, but I see at these tables to-night inorganic and organic chemists, analytical and physical chemists, and not least of all, perhaps, biochemists. I won't suggest that the specialisation which is obviously taking place in your ranks has gone quite as far as the young American medical student of whom Dr. Howe told us in Philadelphia last autumn, who announced his intention of specialising in the ear, but had not made up his mind whether it was to be the right ear or the left. But specialisation there certainly is. Indeed, the foundation of the Society was an act of specialisation in 1841; when the Royal Society was first founded, I find from those

interesting records in *Nature* that the discussions ranged quite easily from naval architecture to the distillation of charcoal, from the anatomy of animal intestines to the discussion of a new digester for the brewing industry. Well, every one of those fields now has its own special society or societies. Specialisation must continue, I imagine, and increase, and yet to me as a layman I think there seems to be a movement in progress which must tend to counteract any disadvantages there might be from excessive specialisation; I mean the obvious tendency for different sciences to co-operate in the solution of the more difficult problems that are in front of you.

Professor Wynne, in his address this afternoon, referred to the Department with which I happen to be connected, and spoke of the share which chemists had undoubtedly had in the movement that led to the establishment of that Department. But I do not think that even you perhaps fully realise how close the link always has been, and I imagine always must be, between any organisation established to encourage scientific research and the chemists. Just look back. Professor Wynne's address was partly concerned in dealing with the review that Professor Meldola took before the war—I think in 1907—of the difficulties of the research worker in this country. Professor Meldola, a Past-President of this Society, was an original member of the Advisory Council of the Department of Scientific and Industrial Research and remained a member of that Council until his unfortunate death. Your new President, Dr. Crossley, is Director of Research to the largest Research Association for Industry that has come into existence since those difficult days of the war, the British Cotton Research Association, and that Association and Dr. Crossley are working in constant and continuous co-operation with the Department. Dr. Slater Price, another officer of this Society, is Director of the British Photographic Research Association; Sir Herbert Jackson, a former Vice-President, is Director of the Scientific Instrument Research Association; Dr. Pickard, a former member of your Council, is Director of the Leather Association; Dr. Scott, a Past-President, is a Director of the Laboratory established by the Department at the British Museum in order to study the best means of preserving antique objects of every kind; and finally there is your Treasurer, Professor Jocelyn Thorpe, who is to-day a member of the Chemistry Research Board of the Department and a member of many of its committees.

Now, my contact with all those distinguished men has made a double impression upon my mind. One is the adaptability of the chemist, and the other is his extraordinary power of penetration. Looking at the Research Association movement which I have

referred to already—incidentally there are twenty-four different industries which have organisations of this kind in this country, and the majority of the Directors of Research of those twenty-four Associations are chemists—I draw the conclusion that they must have great adaptability, because I happen to know that in many cases, and in some of the most outstanding cases, the chemists who have been called to those important posts knew nothing about the industry when they took up the appointment, and for that very reason have brought success. Professor Wynne told you this afternoon that those Associations have been useful because they have opened new posts to young men, and nothing could be more important than that. But I think he might possibly have added that these Associations have done more than that. I will tell you an experience of mine which explains. The other day I was in the largest textile mill in the world, and found that they have quite a large and busy research laboratory, and I was told that the reason that that laboratory had been established was because they had been so convinced of the value of research by the Association of which the firm was a member that they were determined to carry the matter further and have an organisation of their own within the works. That is going on all over the country; so that it is not merely if you look at it simply from the point of view of openings for young men—which after all is not the whole story—it is not merely that the Associations provide openings, but that in increasing measure the firms in the Associations as they come to realise the value of research will need the help of chemists and other men of science. And, sir, their power of permeation! Chemistry, it seems to me, has made its way already into almost every sphere of human life. You dictate to us, sir, what we are to eat, though I believe you are not entirely agreed as to the preservatives that should be used for our food; you give us new textiles to wear—or at least you give our wives new textiles to wear, and when we are ill you indicate to us, attracted as we are by the skilful advertisements of people who are out for that weakness of man that comes with illness, and you tell us where the medicines we are advised to take fail to come up to what they claim to be.

Now, sir, I could quite safely, with considerable safety, go on to tell you of the records of your great men who have been officers and Fellows of this Society. I could refer to the Central Library which you have established, which helps all the Societies connected with chemistry to have a nodal point from which they can gather their recorded information. I could speak of your research fund. I could tell you of the brave efforts you are making in spite of rising prices and a printers' strike to keep the publications going. But

if I did, I should only be telling you what you know far better than I do.

I am going to venture, sir, in view of the most excellent hospitality which you have offered me, and in view of the patience with which you, ladies and gentlemen, have listened to me up to the moment, I am going to venture to be bold, and to tell you how the present state of chemistry strikes a rank outsider.

I remember that when my brother-in-law, more than forty years ago, tried to teach me some chemistry, the molecule seemed to me a much more important thing than the atom. The atom, to my untutored mind, seemed a sort of axiom which you had to accept, but which compared with the interest of the molecule was a poor thing. Now I venture to think that possibly until comparatively recent times chemistry has concerned itself a good deal more with the molecule and its behaviour than with the atom. But is that condition going to last? The other night I heard a distinguished young biologist speaking of several sciences and claim as his belief that the central science of the future would be biology. He was prepared to take off his hat to physics and chemistry as important fundamentally, but the future lay with biology. One did not live in the cellars of a house, but in the upper storey. Well, as an outsider I am bound to say that I doubt that. To me, at any rate, and possibly to other people who are not chemists, chemistry seems to be taking increasingly a central position and bringing to its service the work, the tools, which other scientists on both sides of it are preparing. What has physics done recently from the point of view of chemistry? Has it not, by giving you the anatomy of the atom, and by revealing the structure of the space lattice, helped you to get a picture of three things—first, the mystery of chemical attraction, secondly, as Sir William Hardy, in his Bakerian lecture, pointed out, the phenomena presented by liquid and solid surfaces in close contact, and thirdly, the problem of catalysis. Those things are giving you, are they not, larger control over the speed and nature of reaction? But the engineer similarly is bringing in the tool of high pressure, and what will happen when the knowledge you already have, and these tools you already have, are brought to bear under the conditions of high pressure, it is very difficult to prophesy. And so you are forcing your way into the biological field. Another tool I fancy I see in your hands will be those mysterious accessory vitamins which link up your chemical work with those mysterious chemical reactions of the animal and vegetable organisms.

Well, sir, I have proved my incapacity for proposing this toast, and I will therefore ask you to drink to the health and future of the

Chemical Society, coupling with the toast the name of your President, Dr. Crossley.

Dr. Arthur W. Crossley replied :—

I am sure the Society would wish me to thank you, Sir Frank Heath, very warmly for the way in which you have proposed this toast. My predecessor in this Chair has this afternoon answered, I think, fairly fully some of the remarks which you have made. He has expressed his appreciation of the efforts of the Department of Scientific and Industrial Research. Perhaps, as being somewhat intimately associated with that Department, I may be allowed to add one or two words. So far as my experience goes that Department is free from, shall we say, a Government monopoly—Red Tape, and is willing in every way possible to help anyone interested in the work it is doing. I have had some experience of the professional or professorial side of chemistry, and for the past five years I have had some experience of chemistry as applied to industry. I say, with full consideration of what I am saying, that in my opinion the Department has founded in the Industrial Research Associations a movement which is destined to play an all-important part in the future of this country. By no other means that I can conceive could science have been brought into those industries. I hope on some future occasion to speak somewhat more fully on this subject, and for the present, if you will not think it impertinent on my part, I should like to congratulate the Department on the big efforts which it has started and to say, "Don't be in the least discouraged by disparaging remarks that may be made about you."

I believe it is customary for the President on these occasions to make some reference to the affairs of the Society. This afternoon we had our Annual General Meeting, and by virtue of a decision arrived at, I find things weighing somewhat heavily on my shoulders. I refer to the decision which permits me to have the honour to occupy the position which I do at the present moment.

The election of one President, of necessity, means the retirement of someone who has occupied that post. It falls to more eloquent lips than mine to propose the toast of Professor Wynne this evening. I hope, however, that Professor Armstrong will forgive me if I say one or two words. When the time comes for Professor Wynne to apply for armorial bearings I would like to suggest that he take one single word for his motto, and that word is "Thorough." His sole aim has been efficiency, and in endeavouring to attain it he has not spared himself in the slightest degree. Few realise when he comes to a meeting and quietly says, "I think we should be well advised to do so and so," that this has possibly meant hours of thought, perhaps wrestling with the mystic language of charters and bye-

laws, perhaps the writing of numerous letters and documents. To do the right thing for the Society's welfare has been his sole object. I should like to speak on behalf of us all just one or two words to Professor Wynne. They are simple, but my long-standing friendship with him enables me to know, I think, that he will understand.

"Professor Wynne, we have learned to know something of the time, care and thought which you have expended on our behalf during the past two years. We appreciate; we are grateful."

The Chemical Society is rightly, in the opinion of its Fellows, a very exceptional and uncommon institution, indeed our forbears taught us to regard it as such. They did not found the Chemical Society of London, or England, or of Great Britain, they founded simply "the Chemical Society," and as such we are proud to regard it. We desire no addition: we ourselves are content to be chemists, without the added epithet of druggists which so many kind friends attempt to hurl at us. But I regret to say that when one consideration is taken into account we become quite unexceptional, quite common, and resemble most other societies, institutions, and individuals, inasmuch as we are finding it very difficult to make our income balance our expenditure. Up to the early days of 1914 we were quite a happy band, able to publish the original communications sent in by our Fellows, able to give our Fellows full value for their subscriptions and able to put by a small sum of money each year. In those days a page of the Journal cost 17*s*. 5*d*.; in 1921 the price had risen to £2 12*s*. 4*d*. It is true that at the present moment the price has fallen somewhat, but it is still well above twice the amount that it was in 1914. Moreover, the original communications are always on the increase, and we have now to make annual provision for the publication of 3,500 to 4,000 pages of Transactions alone. The situation is a very serious one from the point of view of the Society and it has given the Council furiously to think as to the possibilities of meeting it. The first step was to increase the subscription of our Fellows by 50 per cent. It is greatly to be regretted that it was found necessary to do so, for the majority of our Fellows are young men, and young chemists—in fact, I think I may say most chemists—are not over-burdened with this world's goods. The second step was to adopt the suggestion of the Treasurer to ask our Fellows to subscribe to a Publications Fund, the interest on which should be devoted to the upkeep of the Journal. We have raised in this way nearly two thousand pounds, but that is not enough, and we were faced this year with a possible adverse balance of some three thousand pounds. The Treasurer this afternoon told us we actually had a credit balance of some £210, but how has this been obtained? By ruthlessly cutting down the original communications

sent in for publication, to such an extent as to cause endless displeasure to authors and to leave it doubtful as to whether we are doing justice to their work; further, by asking Fellows to pay for the Annual Reports, which so far have always been distributed free, and by many other curtailments of our legitimate activities which, in my opinion, are greatly to the disadvantage of our Fellows and form a distinct danger to the prestige of British chemistry. Most societies, most institutions and most individuals themselves decide the pace at which they will live, and the pace is generally regulated by monetary possibilities. But the Chemical Society is again exceptional. The pace at which we are living has not been decided upon by ourselves, but has been decided upon by no less an authority than the nation.

I have stated that up to 1914 we were a happy band. In that year the nation spoke to us for the first time on record, I believe, but it spoke in no uncertain voice. It said, in the first place, "We are at war. We want certain drugs used for the alleviation of pain and suffering; we have so far obtained these supplies from abroad, and that source is now cut off. We are aware that these drugs have never previously been made in this country; we are aware that they require skilled labour for their production. Therefore we want you to prepare them for us." Well, those drugs were prepared by an organised effort on the part of the chemists of practically all the Universities and University Colleges in this country. Then came a second call. The nation said, "We want more explosives: T.N.T., picric acid, ammonium nitrate; we want acetone and dye-stuffs." Finally, there came a third call: "We want poison gas, poisonous and always more poisonous, and with each gas we want complete protection." I do not think it can be said that any of these calls were made in vain, or that the chemists of this country were found wanting in any way. So far as I know the chemists of this country, that is, the Chemical Society has never spoken back to the nation, but I suggest the time has come when this might be done, and in terms such as these :—

"In 1914 you asked us to do certain work for you, which we did to the best of our ability. We at once admit that some of our results were not forthcoming as speedily as we could have wished and in circumstances where speed was all important, due to the fact that the type of work which you asked us to do was new to us and we had perforce to gain experience. This experience has shown us clearly that in order to be prepared for any call which you may make upon us in the future, when delay may prove fatal, it is necessary that nothing should be left to chance, and it is therefore essential for us to carry out numberless researches so as to keep ourselves fully

INFORMATION FOR AUTHORS.

The names of new compounds should be italicised (underlined in the typescript), and the results of analysis given in the form :

> (Found : C, 43·2 ; H, 6·5 ; N, 11·3 ; *M*, cryoscopic in benzene, 276, 258. $C_9H_{16}O_6N_2$ requires C, 43·5 ; H, 6·4 ; N, 11·3% ; *M*, 248).

Only in special cases should full analytical data be recorded.

For known compounds, the results of analysis should be given in the form :

> (Found : C, 50·1 ; H, 11·1 ; N, 39·1. Calc., C, 50·0 ; H, 11·1 ; N, 38·9%).

In giving references to other work, the journal (abbreviated title), the year, the volume, and the page should be given in the text in the order shown ; e.g. *J. pr. Chem.*, 1905, **71**, 260. The official list of abbreviated titles is given at the end of the Annual Index of Abstracts.

informed of the possibilities of chemistry generally. Your requests of 1914 have greatly stimulated research activities in this country, and the publication of the increased number of papers has become a very serious matter to the Chemical Society, which can only meet the present situation by greatly curtailing its legitimate and rightful activities. In these special circumstances, will you not help us to carry on our legitimate work? "

I cannot think that such an appeal could possibly fall on deaf ears, for this very simple reason, that the Chemical Society through the efforts of its members has proved itself to be a national asset of the utmost magnitude and importance. Sir Frank Heath, once more I thank you for the way in which you have proposed the toast of the Chemical Society.

Professor Henry E. Armstrong (Past-President), in proposing "The Retiring President," Professor W. P. Wynne, said :—

Mr. President and Fellows of the Chemical Society, I ask you to lend me your ears and I hope I shall reach them. You have an unusual opportunity, an unusual spectacle, to offer to our guests to-night—that of a retiring President. The programme is wrongly printed. The "The" should be in Clarendon and "retiring" in italics. Presidents are not often retiring. Their business is to be unashamed and aggressive on behalf of the bodies they represent. A little more than two years ago I undertook two tasks: one, an easy one, was to convince the Society, the Council of your Society, that a particular person was *the* man for the office of President; the other, an almost impossible one, to cajole, to persuade, all but to force that particular person to recognise, as the walrus said, that his time was come to take on the many things pertaining to the President's office in our honourable body. It is little short of forty years ago, on March 27th, 1886, that he came to me as private assistant and had we been wise we should never have parted company. The years we worked together were the happiest and most fruitful of my life. We were not called upon to concentrate hydrogen ions; we never wasted time on noughts and crosses; no Lowry worried us with perpetual rechristenings of the already fully-named; we just quietly kept company with a hydrocarbon which was thoroughly well behaved and responsive. Our work was straightforward. There was no angle worship about it and we reported our results without fuss of any kind, in the briefest possible manner.

We put up ten signposts for the Di- and fourteen for the Trichloronaphthalenes and thereby demonstrated the truth of a doctrine fitly to be called, a *theory* of benzenoid structure, which I venture to say no *X*-ray analysis can upset. I think I may say

we were both proud of our exhibit at Wembley last year, when we thought of its implications. Our work pleased the Germans but it met with no recognition at home. It was unnoticed and that was a double compliment. It cost much toil during many years and a good deal of hard cash; neither of us made a halfpenny out of it.

I am told that Mr. Wells asks a couple of hundred pounds for a couple of thousand words. At all times, we could get what we wanted, what material we wanted, free of cost from Germany. We were never offered anything from our English works and our advice and assistance was never invited, although we worked in a technical college. Now, a great branch of the dye-stuff industry stands upon the foundation we built up. Yet neither before nor during the war, nor since, have we been asked to advise or assist in any way in the construction of the English edifice. Now, I modestly mention these points, in support of what the President said to-day as to the lack of co-operation between science and industry. When that address of his is printed, I trust that the measured terms in which he spoke on that subject will have their effect. I may say that the work was done in a sense *sub-rosa*, without official encouragement. I recollect on one occasion speaking to our hon. secretary, Sir John Watney, about research. His immediate reply was, "Your business is to teach boys, not to do research." That is the kind of encouragement we got in those days. This is the spirit that has been behind the comparative failure of our institutions to do original work, of which the President spoke to-day. It was not the primary fault of those who were working in the institutions.

I was glad to hear him speak out particularly on one subject—I think it was the keynote of his address—and say plainly that it is absurd for the Universities of this country all to attempt to do the same thing and on the same scale. Sir Frank Heath has told you of the tendency there is to specialise. A great lesson to be learnt by the Universities in this country is that they too must specialise. His University has no right to deal with anything but iron and steel and things of that kind. It will only be by specialising, that it will be possible for the several universities to effect the exchange of workers of which he spoke. Supposing we were to legislate to-morrow in the direction in which he spoke, all the research workers would drift to one or two places. That is a serious danger of any attempt of that kind.

Now to return to the man. My respect for his great ability as a worker, as a chemist and teacher and for the nobility of his character, has steadily increased with years. As a chemist, I

know of no better worker and teacher; as a man I have known no man so conscientious and self-sacrificing. I would recall to you the service he rendered as Editor in years gone by, of which our President gave so striking an illustration to-day. I wish the spirit he showed on that occasion could be manifest throughout the Society and I wish that Editors could be brought to take the same interest and at the same time show the same ability in their Editorial work that our late President displayed. You have heard how conscientious he has been. He has attended every possible meeting of the Society it has been possible for him to attend and he has done a great deal of outside work. Such a man deserves our thanks, not only for the work he has done, for the direct service he has rendered, more particularly must we thank him for the example he has set. Unsparing unselfishness is scarcely a present failing of the chemist, but the time is at hand when it must be your distinct characteristic.

Sir Frank Heath has rightly told you that after all it is not the atom but the molecule that is the real thing. The atom has no character until it joins up into the molecule. Speaking before the Institute of Chemistry recently, I said that chemists have reason to be proud of themselves on account of their achievements. At all events, the young women of the day are clad in cellulose and fine raiment mainly through your services. Even the Medical Research Council is faintly yearning for chemical aid. Sir Frank Heath spoke of Biology being the science of the future. Biology is nothing but chemistry when it comes to the real thing. Biology is making slow progress at the present time but most of the Bio-chemists, as I have said, are but bits of chemists. When they become chemists, there will be a real advance in vital chemistry and in medicine too. Still, with all this service to your score you have no recognised public standard and what is worse, no internal cohesion but lots of friction. You are not three hydrocarbons but more than thirty. Now is the time for you to show that you can come together, hold together, log roll together and organise together. There must be complete fusion of interests, I hold; an end must be put to the present chaos and inefficiency of publication. If necessary, to find funds, you must give up smoking. Your analyses will be more trustworthy if you do. There will be less tendency to believe in the transmutation of copper into lithium. No small temporary scheme will suffice. To be at all, you must be big.

Now, gentlemen, if you have any element of human feeling, you will sympathise with me in my determination to overcome to-night the modesty of your too-retiring President and join with

me in thanking him, with all possible warmth, for the distinguished way in which he has served the Society during the past two years and for the great example he has set by his unselfish devotion to the interests of our profession. I call upon you to join with me in drinking the future health and happiness of our late President, Professor Wynne.

Professor W. P. Wynne, D.Sc., F.R.S., responding, said :—

I rise to thank you most heartily for the cordial way in which you have received the toast. I hope I may be allowed to regard it not as applying only to myself, but as including all those who have worked with me in the interests of the Society during the past two years. But for the loyal co-operation and cordial support of the officers, the Council and the office staff I could have done little or nothing, despite all the kind things Professor Armstrong has said in proposing the toast. He is my father in chemistry, and his eulogy is to be explained not by my merit but by the partiality often displayed by a parent.

As a father, Professor Armstrong is doubly fortunate, for, in addition to four distinguished sons who bear his name, he has a numerous chemical family of which I am proud to be the eldest. Two others of us, Sir William Pope and Professor Lowry, are also present this evening. As will have been gathered from what he said we may not be in complete agreement with our father's views on every subject—a not uncommon experience in families, chemical or otherwise—but that does not diminish in the slightest degree our affection for him or sincere appreciation of our fortunate upbringing.

Professor Armstrong referred to the date on which I became his private assistant. I had left South Kensington a few months earlier, and it was through Professor Japp's kind offices that this most happy chance came my way. If a reference may be permitted to the plea put forward this afternoon for the encouragement of migration, this crossing of Exhibition Road from the one College to the other did undoubtedly exercise a profound influence on my own career.

I had the good fortune to number among my teachers no fewer than seven Fellows of the Royal Society, five of them being Past-Presidents of this Society, and, on an occasion such as this, it is no less a pleasure than a duty gratefully to acknowledge my deep indebtedness to them. The first of these Fellows was Dr. George Gore, who, it may be remembered, published so long ago as 1865 an account of the modification in the properties of some seventy substances produced by complete desiccation, and thus was a pioneer in the field of research so closely associated with Professor

Brereton Baker's name. He was a self-made man. How he came to be chemistry master in King Edward's School, Birmingham, I do not know, but he had never been to a training college, and thus his originality had not been educated out of him. His method of judging the nature of our work was to suggest at the commencement of the class, that we should write a résumé of the previous lesson. This was assessed by the number of pages handed in at the end of a quarter of an hour, irrespective of the fact that some of them might contain six words and some of them sixty. That is the way in which I started to learn chemistry. Then, having left school, I went to evening classes after the day's work, and am a product of that system of " payment by results," under which science classes were farmed out to teachers, who were paid by fees based on successes achieved by their students in the examinations conducted by the Science and Art Department of those days. Despite the hard things which have been said about it, I do not think the system was wholly bad. At any rate it gave me my chance and to many others theirs. It provided, indeed, the only avenue to instruction in science subjects open to most students in the 'seventies of last century before University Colleges and Technical Schools came into existence. By its aid I went to South Kensington in 1881 and there had the great advantage of being a student under Sir Edward Frankland, Professor Percy Frankland and Professor Japp, who began my training in research. Thereafter followed the training as a teacher under Professor Armstrong, who taught me—nay, compelled me—to think; Sir Edward Thorpe, who brought me back to the old College, and Sir William Tilden, who last year, although in infirm health, did me the great honour of coming to the anniversary meeting and saying words which I shall never forget. I am to see him to-morrow, and I hope I may take to him from this gathering a message of affectionate regard and esteem. (Cheers.)

There is just one remark I should like further to make. Sir Frank Heath spoke in most appreciative terms of chemists and of their adaptability, for which we thank him. But it is only right to remember that the indebtedness to which he referred is not wholly on one side. I think the signal success which has attended the work of Sir William McCormick and Sir Frank Heath, neither of them men of science, in producing the result known as the Department of Scientific and Industrial Research, serves to show that success in such enterprises comes not only from a knowledge of men and affairs, but in no small measure from a sympathy with, followed by an understanding of, the type of problem to be solved.

As the thirty-ninth President, no longer retiring but retired, I salute my friend and colleague, the fortieth President, wishing him

as happy a time during his period of office as fell to my lot. Once again I thank you all most sincerely for the way in which the toast has been received. I do not deserve the praise; I have simply done my job.

The toast of "The Federated Societies" was given by Professor Irvine Masson, who said:—

There are, I suppose, few of us here who are so deeply learned in chemical politics as to be at once aware of what this term connotes; and I will therefore first adopt the old-fashioned plan of giving instruction by means of enumeration. The Chemical Society is affiliated with no fewer than seventeen others. Of the eighteen, four deal primarily with pure science—the Mineralogical, Faraday, Biochemical, and ourselves; twelve with the methods and the discoveries of pure science as applied to practical arts, namely the Society of Chemical Industry, Society of Public Analysts, Royal Agricultural Society, Institute of Brewing, Society of Dyers and Colourists, Society of Leather Trades' Chemists, Royal Photographic Society, Institute of Metals, Iron and Steel Institute, Ceramic Society, Society of Glass Technologists, Institution of Gas Engineers; and two are of a special character, namely, the Institute of Chemistry and the Association of British Chemical Manufacturers, which deal with chemists professionally and in their relation to the lay public.

What is especially made prominent by this list is, not so much the subdivision of pure chemistry, as the great number of ways in which the science as a whole has found a place in the business concerns of the nation. So evident is this, indeed, to chemists, that we have now and then to remind ourselves that if we have won the privilege of helping a little in the material welfare of our country, we cannot evade the responsibility which has thereby been entrusted to us. And, with this in view, the more we can do to foster intellectual sympathy between all kinds of chemists, the more will our science be able to serve the nation at large. And this is why there is a Federation of all these societies: it is a federation primarily *pro bono publico*, not merely *pro bono chemico*.

Let me indicate briefly two or three ways in which co-operation has usefully shown itself at present.

The Library of the Chemical Society has of late years been extended and is annually increased, with the set purpose of being useful not alone to its own Fellows but also to members of the other affiliated societies. Towards the heavy annual cost of this addition to its original function, many of these Societies have contributed; and now our Library, poorly housed though it is, is becoming a truly national asset. Last year, for instance, the

visits to consult our 30,000 volumes averaged about twenty-two per day; and of these, one-third of the consultations were made by members, not of the Chemical Society, but of other societies, while among the other two-thirds many were members of the Chemical Society and the others as well.

Another example is seen in the co-operation between the Chemical Society and the Society of Chemical Industry which has set going the Bureau of Chemical Abstracts. The Bureau has done a great deal of quiet work already, and it has before it the central problem of unifying the British publications which survey each month or fortnight the whole of the world's current literature of chemistry. Surely no obstacle short of insuperable bankruptcy should be allowed to stand in the way of an end so desirable.

A collective token of federation is, I take it, to be seen in that body of delegates, the Federal Council for Pure and Applied Chemistry. There is something in this Council which reminds one of the luminiferous ether. It was originally invented to offer a medium for the propagation of light and radiation of energy, and to overcome the difficulty of action at a distance. Yet, I have been told, experiments made with the object of detecting it in motion have failed; and some daring moderns have even questioned the necessity for believing in it, and have dubbed it a pure convention.

Now there is a name which I have to couple with this toast—that of Mr. Woolcock. Chemists, as such, are trained to deal with things which are in themselves non-human; yet, because these things, and we ourselves, must everywhere affect human affairs, we need human guidance. It is to wise and experienced men like Mr. Woolcock that we instinctively turn for such help; and not one of you does not know how well and generously Mr. Woolcock gives it—think of one example alone, chemistry at Wembley. Mr. Woolcock fulfils the function of an ideal catalyser; for he starts, facilitates, or hastens actions, without upsetting any equilibrium, and himself emerges apparently unchanged at the end.

I ask you to couple with the toast of the Federated Societies the name of Mr. Woolcock.

Mr. W. J. U. Woolcock in his reply stated :—

I feel my efforts to respond to this toast will be somewhat inadequate, the more so as on looking at the toast list and seeing the term, "The Federated Societies," I did not know what was meant by it. My chemical education is, as you know, very limited. Hitherto I have supposed that I knew just sufficient chemistry to understand what the real chemist was talking about when I had to take his advice. For once I have failed. Professor Masson, convincing as

he is on most subjects, lucid to a fault on his own particular subject, has left me absolutely in the dark as to what is meant by the "Federated Societies." I at first thought that possibly it was a misprint and that Sir William Pope was intended to reply on behalf of the Federal Council. The delightful language in which Professor Masson brushed on one side the Federal Council leaves me in no doubt that he is not referring to that body, but he gave us, in order that we might know exactly about what we are talking, a list of learned bodies which, in the hope or in the anticipation of the Chemical Society, will ultimately become federated. Let us hope that that will eventuate. In future when I have to think of a reason why I should be considered a chemist, I shall always think of what Sir Frank Heath said, and regard adaptability as a qualification in a claim for that distinguished name, because I think it is a qualification which those of us who lack some qualification in science may readily embrace and regard as practicable, and in that way seek admission to the inner circle, because it is very true that the chemist is an adaptable person, and those who have to have something to do with him need to be adaptable as well.

It has been my fortune during the past twelve months to study two chemists at very close range. In fact, if I had attempted to define the Federated Societies I should have thought of a rather shorter list, and thought of the Chemical Society, the Institute of Chemistry and the Society of Chemical Industry, because of the real federation which has existed between those three bodies for some little time, and perhaps never more closely than during the past twelve months. I have been able to study at short range the Presidents of the Chemical Society and the Institute of Chemistry. We have travelled together, and it is a common thing for Professor Henderson and myself to speak together in different towns. That kind of intimacy brings familiarity and a working together which can only be obtained in that way. I remember that some time ago we arrived in Birmingham together. We had been in Glasgow the night before and had as usual said the proper thing about each other. Professor Henderson, when we got to Birmingham, called my attention to a placard just outside the station, and, after a quick glance, said, "They know we are coming," but not taking it quite as quickly as Professor Henderson, I saw that he was mistaken and I studied it a little more closely. The two Macs advertised there were not ourselves.

During the past twelve months there has been hardly a local branch of the Society of Chemical Industry or of the Institute of Chemistry that has not had a joint dinner. This indicates a desire for co-operation among the rank and file of which those who are

temporarily the leaders of the chemical societies and associations in this country will have to take notice.

I do not myself believe it is possible for the Councils of the various Societies to lay down a definite scheme for federation and to attempt to impose that on the local branches of the various Societies, but I do think that at the present time there is a demand throughout the country that we shall do something to prevent this appalling overlapping and duplication in the production of chemical literature, and do something which will satisfy the man who likes to consider himself in the rank and file and who at the same time feels that there is a definite need for a closer union among the Societies and the Associations.

Well now, neither Professor Wynne nor Professor Henderson nor myself is capable of doing that sort of thing individually. Together, of course, we have found it very easy. If we were upon a job which required modesty of demeanour, Professor Palmer Wynne did it. If it required some of that native shrewdness and ruggedness of character, Professor Wynne and I pushed Professor Henderson into it. If, of course, it were a mere torrent of words that was required, you know what would happen. But unlike the Duke of Plaza Toro, we have no desire to lead our Societies from behind, and in our individual capacity—not in our representative capacity—we have prepared a scheme for a Chemistry House to which each of us felt entitled to put his name, not binding our respective Societies or Associations in any way. This is a scheme which we feel we can recommend to those of our friends who are prepared to listen to our recommendations. I feel that with you, Dr. Crossley, in the chair in succession to Professor Palmer Wynne—and if I may say so, I welcome you very heartily in the chair—the work will continue.

We of the "Federated Societies," yes, of the Federated in inverted commas Societies, thank you very much indeed for inviting us to-night, and thank Professor Masson for proposing the toast. We wish the Chemical Society every prosperity during the coming year, and hope that the traditions which have been built up during the past four or five years of close working and co-operation between the officers of the various Societies will be maintained. We trust that under your guidance those traditions will continue and we may be even more successful in the coming year than in the past.

Professor F. G. Donnan, C.B.E., D.Sc., F.R.S. (Foreign Secretary), proposed the toast of "The Guests," coupled with the names of Professor Ernst Cohen, of Utrecht University (representing the Nederlandsche Chemische Vereeniging), and Mr. J. Hunter Gray, K.C., M.A. He said :—

We have here to-night four distinguished representatives of

Holland, Professor H. J. Backer, Professor Ernst Cohen, Professor A. F. Holleman, and Professor H. ter Meulen. Three of them are accompanied by their wives. May I say that we wish these ladies also a very hearty welcome to London and to the Chemical Society dinner.

I believe it is true that although the population of Holland is relatively small, actually the largest number of Nobel prizes has been given to that nation, which is a wonderful tribute to the scientific output and ability of Holland. It is nothing new, for that country has always been perhaps the greatest centre of scientific culture in Europe. I have great pleasure in saying a few words about my friend Professor Cohen, of Utrecht, whose name I have the honour to couple with this toast. I think it is rather late in the evening to refer to the distinguished work of Professor Cohen, but he is the most eminent pupil of that great man, Professor J. H. van't Hoff, and is one of the greatest authorities on the effect of high pressure on chemical reactions, and many other things.

When I come to look at the list of other distinguished guests associated with this toast, I feel like a miserable sinner transported to Paradise and asked to propose the toast of all the holy Saints. The Rt. Hon. Sir John Anderson, G.C.B. (Permanent Under-Secretary of State for Home Affairs), is one of our guests, and may I assure him, speaking as one Secretary of State to another, that if in the conduct of the affairs of this great country he wishes for any advice, the President of the Chemical Society will be always willing to help.

I have also the pleasure of coupling with this toast another name, that of one of those modest men of law, Mr. J. Hunter Gray. I have had the honour to be associated with him in one or two cases. It is needless to speak about these great men, because we all spend our nights reading the *Evening Standard*, and our days reading *The Times*, and we have the greatest admiration for their work.

There is one thing I should like to say before I conclude, namely, in reference to a very important part of the toast, that of the ladies present to-night. We wish them all a very hearty welcome.

It is my great pleasure and honour now to give you the toast of "The Guests," coupled with the names of Professor Cohen and Mr. Hunter Gray.

Professor Ernst Cohen, who replied for the Dutch chemists present, said :—

During the toast of my friend Donnan I made some notes, but it seems to be impossible to make a response to all the remarks he made in the toast. I think it would take too much time. This afternoon I had a warning from the new President of your Society

that everyone must be brief. I think there is no nation more fond of conciseness in speech than the English. Take, for instance, your chemical abstracts. When an English chemist wants to describe the properties of any substance or fluid he says: B.P. 100, F.P. zero, D.C. 80, and for those who are not familiar with those telegraphic hieroglyphics I will add that B.P. means boiling point, F.P. freezing point, D.C. dielectric constant.

In English literature or poetry you find absolutely the same thing. I remember an English rhyme made up of initial letters which, for those who are not in a hurry, I will translate:

A fishy old fisher, called Fisher,
Fished fish on the edge of a fissure.
The fish with a grin
Pulled the fisherman in.
Now they're fishing for the Fisher within.

But the most striking conciseness is found in the language of English daily life. When I have to write a letter to the Foreign Secretary of the Chemical Society I write: F. G. Donnan, M.A., Ph.D., F.R.S., F.S.C.S., London, W.C.1, and so I could go on. If I were to follow these lines in responding, I would have to condense them into a few initials, which in plain English would mean, "I wish to the Council and the Fellows of the Chemical Society, good luck, welfare, prosperity and happiness."

Ladies and gentlemen, as I am a foreigner, you will allow me to express myself in a somewhat more elaborate way. In the first place, I have to thank the Council and the Fellows of the Chemical Society in the name of my Dutch colleagues who were so kindly invited to attend this dinner and the Annual Meeting this afternoon, and also to thank you in the name of the Dutch Chemical Society whose representatives are prevented from being here and celebrating with you the birthday of this Society with which so many illustrious names are linked.

There is a French saying which means, "Every meeting we finish by a dinner whenever we can, and it is by a dinner that we rule over man." But I make an alteration in the last line and say, "It is our dinners which delight ladies and men." The question arises as to the origin of the custom of finishing such a meeting with a dinner. We have had two dinners to-day; in the afternoon our President gave us mental food in his most interesting lecture, and now we have material food. Whence comes the custom of linking the two? It is your countryman, Joseph Priestley, to whom you are indebted for this most pleasant custom. Priestley has been pictured in a fascinating way in a caricature by one of your countrymen as sitting at a dinner, but at a dinner which he never attended.

Priestley was a very wise man. He also invented soda-water, a very good remedy for many persons who have attended a dinner. I have been so lucky as to find the caricature, and I have had it copied and will ask you all to accept a copy not only as a memento of this splendid invention by your countryman, but also as a memento of most pleasant hours spent in your company. I feel sure that my Dutch colleagues will feel with me that we have had a very interesting meeting and enjoyable dinner with you, and thank you all for the very kind way in which you have invited and entertained us.

Mr. J. Hunter Gray also replied, saying :—

Professor Donnan, and members of the Chemical Society, a few days ago I had the burden and privilege to make the last speech at another meeting and I had taken the greatest trouble to prepare an impromptu speech to deliver on that evening. It passed through my mind that I might palm it off once more, but I had no sooner come into this room than I found two members of this company—Sir Frank Heath and Professor Armstrong—who had heard my last impromptu effort. Therefore I am thankful I had made preparations for another impromptu speech.

This toast recalls to me a set of questions and answers which appeared recently in one of the newspapers. The publication of those questions and answers was for the purpose of demonstrating the super-excellence of a system of education in this country for which we paid so many millions of pounds annually. One question put was, What is a Guest? One bright youth answered, "A Guest is a joke." Well, I hope the guests are not worse than jokes to-night, because I would rather be a guest than a nuisance, especially as I am making the last speech on the toast list. The guest who talks too much is apt to become a nuisance, so I will be quite brief. Another answer was, "A Guest is a person usually of the male sex who eats and drinks as much as he can and pays nothing for it." I suspect that the young person who wrote that answer was a precocious member of the other sex. But we do, as guests, come within that definition.

We to-night are guests of a most eminent body of scientific men, and it is inevitable that our thoughts should be extraordinary when we hear about molecules and atoms and the somewhat dubious relationship between them, and we may play with unusual ideas. For example, usually when I look at the menu and note the various courses and I see there is one course entitled *Saumon d'Écosse* with some other French words, I should say that was good Scotch salmon. But no such thoughts came into my mind to-night. When I put my knife into that salmon, I wondered if I should find at least a dozen of those bodies Sir Frank Heath referred to, vitamins,

running about, and perhaps I might even find a few of those bodies known by some curious names, and see the poor little vitamin running away and calling in terror-stricken tones, " Yadil, Yadil."

But let me be serious. I am not one of those, although a mere lawyer, who think that the premier gifts of scientific genius have departed from this country. I believe that in the future, as in the past, our British men of science will remain in the van of scientific progress. The whole world has marvelled at the wonderful work done by them, and especially, may I say, by our chemists in the Great War, and believing, as I do, that any future warfare will depend more and more upon scientific progress, I have no fear, if only the public and the Governments of this country will give to science that encouragement which it demands and which it deserves.

I am proud to be associated with the great scientist Professor Cohen to-night in responding to the toast of the Guests. We, the Guests, thank you, our Host.

Ordinary Scientific Meeting, Thursday, April 2nd, 1925, at 8 p.m., Dr. Arthur W. Crossley, C.M.G., C.B.E., D.Sc., F.R.S., President, in the Chair.

The President referred to the loss sustained by the Society, through death, of the following :

Honorary Fellow.	Elected.	Died.
Guglielmo Körner	Jan. 20th, 1898.	March 28th.
Fellows.		
Charles Samuel Mummery	Dec. 5th, 1907.	March 27th.
Robert Atkinson Oddy	Feb. 21st, 1918.	March 12th.

The President announced :

1. That the Keith Gold Prize Medal of the Royal Society of Edinburgh awarded to the late Robert Traill Omond, LL.D., has been lent by Mr. Arnold Stevenson for exhibition in the Medal Case. It is hoped that other Fellows will add to the interest of the Society's Collection by loan or gift.

2. That the following Committees for 1925–1926 had been appointed by the Council :

Finance Committee : J. L. Baker, A. Chaston Chapman, F. P. Dunn, C. A. Hill, G. T. Moody, R. H. Pickard, and the Officers (Treasurer as Chairman).

House Committee : J. L. Baker, Sir Herbert Jackson, Alexander Scott, J. M. Thomson, Sir William Tilden, E. W. Voelcker, and the Officers.

Library Committee : P. P. Bedson, O. L. Brady, J. R. Partington (Chairman), Sir Thomas K. Rose, Alexander Scott, J. F.

Spencer, the Officers, and the Librarian, together with the following representatives of contributing Societies : J. L. Baker, R. B. Brown, J. C. Drummond, A. Harden, J. P. Longstaff, R. L. Mond, G. Senter.

Publication Committee : H. B. Baker, E. C. C. Baly, H. Bassett, O. L. Brady, H. W. Dudley, U. R. Evans, J. J. Fox, A. J. Greenaway, I. M. Heilbron, T. A. Henry, C. K. Ingold, H. McCombie, I. Masson, W. H. Mills, T. S. Moore, G. T. Morgan, J. R. Partington, J. C. Philip, R. H. Pickard, F. L. Pyman, N. V. Sidgwick (Chairman), W. P. Wynne, and the Officers.

Research Fund Committee : A. J. Allmand, H. B. Baker, E. C. C. Baly, J. B. Cohen, W. H. Mills, Sir Robert Robertson, R. Robinson, N. V. Sidgwick, Sir James Walker, W. P. Wynne, and the Officers.

The following were formally admitted Fellows of the Chemical Society : G. E. Gardam, G. E. Watts.

Certificates were read for the first time in favour of :

Neville Melton Bligh, A.R.C.S., A.I.C., 67, Castle Road, Bedford.
Hugh Alexander Millar Borland, M.Sc., A.R.C.S., 14, Cotham Road, Bristol.
Malcolm Sinclair Gaskill, 3, Buckingham Road, Hilton Park, Prestwich, Manchester.
Norman Hamer, Ash Mount, Holcombe, Manchester.
Ivor Gray Nixon, 75, The Vale, Golder's Green, N.W. 11.
Vincent Joseph Occleshaw, M.Sc., A.I.C., 22, Byrn Street, Ashton-in-Makerfield, Wigan.
Leon Rubenstein, B.Sc., 87, Eaton Grove, Swansea.
Alec Thomas Streather, B.Sc., A.I.C., 3, Wellington Road, Watford.
Violet Corona Gwynne Trew, 18, Adam Street, Portman Square, W. 1.

The following papers were read :

"The formation of *d*-2 : 2 : 4-trimethyl*cyclo*hexan-3-one-1-carboxylic acid from *d*-camphorquinone." By C. S. Gibson and J. L. Simonsen.

"Aromatic esters of acylecgonines." By W. H. Gray.

"The decomposition of hydrogen peroxide by cobaltic hydroxide." By F. G. Tryhorn and G. Jessop.

RESEARCH FUND COMMITTEE.

A meeting of the Research Fund Committee will be held in June next. Applications for Grants, to be made on forms which can be obtained from the Assistant Secretary, Chemical Society, Burlington House, W. 1, must be received on or before Monday, June 1st, 1925.

All persons who received grants in June, 1924, or in June of

any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be returned by June 1st.

PUBLICATIONS FUND.

In connection with the Appeal for the Publications Fund issued by the Treasurer, it has been decided that a list of donations and subscriptions received shall appear in the Proceedings for June. All donations and subscriptions received prior to the end of May will be included in the List.

LIST OF FELLOWS, 1925.

It has been decided to print the List of Fellows for 1925 and to supply the List to those Fellows who make application to the Assistant Secretary by the 31st July, 1925.

BERICHTE, 1915 to 1924.

Sets of the Berichte from 1915 to 1924 (10 years) are now offered to Fellows of the Society at £22, carriage extra. Application should be made to Mr. S. E. Carr.

List of Papers, or Abstracts thereof, received between March 20th and April 2nd, 1925. (This list does not include the titles of papers which have been read at a Scientific Meeting, or which have appeared in the Journal.)

"The thermal decomposition of ammonia upon various surfaces." By C. N. Hinshelwood and R. E. Burk.

"Strychnine and brucine. Part III. The position of the methoxyl groups in brucine." By F. Lions, W. H. Perkin, and R. Robinson.

"Compounds of tervalent molybdenum. Part III. New oxalates." By W. Wardlaw and W. H. Parker.

"The composition of starch iodide." By H. D. Murray.

"Note on the atomic volume of manganese." By A. N. Campbell.

"Note on molybdenum semipentoxide." By W. Wardlaw and F. H. Nicholls.

"The action of hydrogen chloride on *cyclo*hexylideneazine and on *cyclo*pentylideneazine." By W. H. Perkin and S. G. P. Plant.

" The constitution of soap solutions in the presence of electrolytes : sodium laurate and potassium chloride." By W. C. Quick.

" The tautomerism of dyads. Part III. The effect of the triple linking on the reactivity of neighbouring atoms." By E. H. Ingold.

" The molecular condition of phenol in benzene solution." By J. C. Philip and C. H. D. Clark.

" The solubility of sulphur dioxide in water and in aqueous solutions of potassium chloride and sodium sulphate." By J. C. Hudson.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE BALLOT TO BE HELD AT THE ORDINARY SCIENTIFIC MEETING ON THURSDAY, MAY 7th, 1925.

Bjerrum, Niels Janniksen, Copenhagen, Vendersgade 28. Danish. Professor in Chemistry at the Royal Veterinary and Agricultural College in Copenhagen. Researches on liquid potentials, on complex compounds, especially of chromium, on the ionisation of electrolytes, on the thermic dissociation of water and carbon dioxide, on the theory of titration, on the atomistic explication of ultra-red spectra, etc. (*Signed by*) F. G. Donnan, J. N. Collie, W. E. Garner.

Blunsden, Archibald Beresford, " The Bungalow," Westbury-on-Trym, Bristol. English. Asst. Tech. and Analytical Chemist. Employed for over five years by The British Oil and Cake Mills, Ltd. (Bristol branch) in research, etc., in their laboratory and works. Evening study at the Merchant Venturers Tech. College, including lectures, advanced analysis, and research. City and Guilds of London Institute Final Certificate (Technological) in Oils, Fats, and Candle Manufacture. National Certificate in Chemistry. Desire to keep up-to-date with advance in the scientific world. (*Signed by*) Arthur Marsden, M. W. Jones, Chas. J. Waterfall, S. Siddons Wilson.

Blyde, Geoffrey Alger, " East Cliffe," East Bank Road, Sheffield. British. Steel Maker at A. Blyde & Co., The Wallace Steel Works, Sheffield. Late Student of Metallurgy, Applied Science Department, The University of Sheffield. I am desirous of joining with a view to extending my knowledge of Chemistry and Metallurgy by the use of the Society's Library and Journals. (*Signed by*) John Evans, L. Archbutt, J. E. A. Blyde.

Bowles, Thomas Henry, " Allandale," Meadowside Rd., Cheam, Surrey. British. Chemist, 1st Grade, Government Chemists' Department. 28 years Government Chemists' Department. (*Signed by*) R. Robertson, Geo. Stubbs, J. J. Fox.

Brindley, William Harrison, 11, Millmoor Terrace, Glossop, Derbyshire. British. Demonstrator in Chemistry, Faculty of Technology, University of Manchester. M.C., M.A. (Cantab.), M.Sc.Tech. (Manc.), A.I.C. Demonstrator as above since 1921. Joint author of " An Attempt to Resolve Quaternary Phosphonium Compounds," and " Some Esters of Anisic Acid." (*Signed by*) Frank Lee Pyman, Fredk. M. Rowe, John K. Wood.

Buchan, James Lindsay, Hampden Club, London, N.W. 1. British.

Physico-chemical Research Student, University College, London. B.Sc. (Lond.), Hons. Chemistry. (*Signed by*) F. G. Donnan, W. E. Garner, D. McKie.

Bull, Frank Henry Charles, 50, Cornwall Road, Bishopston, Bristol. British. Works Chemist in the employ of Bristol Gas Company, Bristol. B.Sc. degree 1916 (Bristol University) (Subjects: Chemistry, Physics, Mathematics); Associate of the Institute of Chemistry, 1919; Full Technological Certificates in Gas Engineering and Gas Supply from City and Guilds of London Institute, 1923—4. (*Signed by*) F. Francis, J. W. McBain, M. E. Laing.

Butler, John Alfred Valentine, "The Potteries," Winchcombe, Glos. British. Assistant Lecturer in Chemistry, University College of Swansea. M.Sc. (Birmingham), 1922. Author of papers: *Trans. Faraday Soc.*, **19**, 659, 729, 734, 1924; *J. Phys. Chem.*, **28**, 438, 1924; *Phil. Mag.*, **48**, 746, 927; *Zeits. phys. Chem.*, **113**, 279, etc. *J.C.S.*, 1923, pp. 2370, 2380; 1924, pp. 963, 1101 (jointly with other authors). (*Signed by*) G. T. Morgan, S. R. Carter, J. E. Coates, L. E. Hinkel, E. E. Ayling.

Byford, Annie Lavinia, 73, Elderton Rd., Westcliff-on-sea, Essex. British. Student of Chemistry. B.Sc. (Pass). Studying for B.Sc. Honours in Chemistry at Bedford College for Women. (*Signed by*) J. F. Spencer, H. Crompton, P. V. McKie, E. R. Levy.

Clegg, James Herbert, "West Cliffe," Queens Park Rd., Burnley. British. Engineer and Manager, Burnley Corporation Gas Dept. Member of the Institution of Gas Engineers. My object in seeking membership of your Society is to extend my knowledge of and assist in the furtherance of Chemical Science. (*Signed by*) Raymond Ross, Ernest Hardiker, J. P. Leather.

Cockroft, Horace Cecil, 6, Highfield Terrace, Halifax. British. Schoolmaster. London, B.Sc., 2nd Class Hons. Chemistry, 1922; Associate of the Institute of Chemistry, Jan. 1923; Student at University College, Reading, 1919—1922. Research work on CuCN–KCN–H_2O system incorporated in paper, Bassett and Corbett, *J.C.S.*, Vol. **125**, 1924. (*Signed by*) Robt. D. Abell, H. Bassett, J. W. Dodgson.

Coyne, Francis Xavier, 160, Addison St., Blackburn, Lancs. English. Student at the Blackburn Technical College. Three years' work at a Manufacturing Chemist's as a chemist, in the laboratory. Proficiency in Chemistry, Physics, Mathematics, German, French, Latin, and Greek. (*Signed by*) G. W. F. Holroyd, Harry G. Leigh, Robert H. Pickard.

Craik, James, The University, St. Andrews. British. Carnegie Research Fellow. M.A. 1920 (St. Andrews). B.Sc. 1921 (St. Andrews). Ph.D. 1924 (St. Andrews). Author of a paper entitled "The Mechanism of the Oxidation of Typical Carbohydrates with Hydrogen Peroxide and Hypochlorous Acid," *J. Soc. Chem. Ind.*, 1924, **43**, 171. At present engaged in Research Work in the Chemistry Department, University of St. Andrews. (*Signed by*) J. C. Irvine, John Read, G. M'Owan.

Dane, Herbert Greetham, The Diocesan Training College, Winchester, Hants. British. Tutor and Lecturer (and Demonstrator) in Chemistry at the Winchester Training College. B.Sc. with First Class Honours in Chemistry, Sheffield, 1922. M.Sc. (Sheffield) 1923. Worked under Dr. J. Kenner 1921–22 on the Influence of Steric Factors on Intramolecular Condensation, see J. Kenner and E. Witham, *T.*, 1921, 1452. (*Signed by*) W. P. Wynne, F. G. Tryhorn, Arthur W. Chapman.

Dean, Harry, 134, New Lane, Oswaldtwistle, nr. Accrington. English.

Textile Chemist and Colorist. Assoc. Manchester Coll. of Technology (Bleaching, Dyeing, and Printing, including advanced Organic Chem. and Dyestuffs Intermediates). 3rd year College Certificate of Blackburn Tech. Coll. (Inorg. and Organic Chem. and allied subjects). (*Signed by*) Percy J. Rhodes, G. W. F. Holroyd, E. Knecht.

Dixon, Margaret Stedman Leonora, Homebush, Worcester Rd., Sutton, Surrey. British. Student. A student taking a B.Sc. Honours Degree in Chemistry at Bedford College for Women (University of London). (*Signed by*) J. F. Spencer, H. Crompton, P. V. McKie.

Farnell, Robin George Westbury, Exeter College, Oxford. British. Chemist to the British Empire Sugar Research Association, 3, 5, 7, Old Queen St., S.W. 1. A.R.C.S. A.I.C. Research into the colloidal constituents of the juice of the sugar cane. (*Signed by*) James C. Philip, M. A. Whiteley, H. B. Baker.

Faulkner, Irvine John, Emmanuel College, Cambridge. British. Research Student. (*Signed by*) T. M. Lowry, R. G. W. Norrish, L. P. McHatton.

Flett, Thomas, Anchor Cottage, Kirkwall, Orkney. British. Chemist. At present Works Chemist in a Factory. 4 Years' Course at Glasgow University, 1919—1923; Graduated B.Sc. (Applied Chem.) and was elected A.I.C., 1923; Works chemist at Thornley Binders, Ltd., since January 1924. (*Signed by*) G. G. Henderson, T. S. Patterson, R. Wright, S. Horwood Tucker.

Gardner, Thomas James Elijah, 12, Bushwood Road, Kew, Surrey. English. Works Chemist (Consol Products, Ltd., Sunbury Common, Middlesex). 30 Years' experience in Manufacturing Chemistry, especially in the investigation and perfecting of Synthetical Essences and like products. I am anxious to keep in touch with the developments of modern Chemistry, particularly as applying to my own work. (*Signed by*) Francis W. Hodges, Frank A. Boys, Archibald Macpherson.

Garran, Richard Randolph, Orphir, St. George's Rd., Toorak, Melbourne, Australia. Research student at the University of Melbourne. Bachelor of Science (Melbourne), 1st class Honours and Exhibition in Chemistry in first and second years, 2nd class in third year. Has since done a year's research (heterogeneous equilibrium) and is at present reading for Final Honour Examinations in Chemistry. (*Signed by*) A. C. D. Rivett, E. J. Hartung, W. Davies.

Giblin, John Charles, 3, Kensington Terrace, Brecon, Wales. British. Science-master, Christ College, Brecon. Bachelor of Science (London, 1st Hons. Chem.). Associate of the Institute of Chemistry. (*Signed by*) W. J. Jones, Claude M. Thompson, E. P. Perman.

Gilchrist, Helen Simpson, 82, North St., St. Andrews. British. Research Chemist, Food Investigation Board, D.S.I.R. B.Sc. (St. Andrews), 1917. Ph.D. (St. Andrews), 1921. Author of a thesis on "The Preparation and Constitution of Synthetic Fats, containing a Carbohydrate Residue." Assistant in Chemistry, The University, St. Andrews, 1918—21. Joint author, with Principal Irvine, of (1) A Synthetic Fat, etc., *T.*, 1924, **125**, 1. (2) Condensation of Mannitol with Olive Oil, *ibid.*, 10. (*Signed by*) J. C. Irvine, John Read, G. M'Owan.

Hadfield, Isabel Hodgson, 65, Langham Rd., Teddington, Middlesex. English. Research Chemist. M.Sc., London University. Seven years' research work for the Aeronautics Advisory Committee. Member of the staff at National Physical Laboratory. (*Signed by*) Guy Barr, L. L. Bircumshaw, J. T. Hewitt.

Halpin, James Francis, St. Chads, 39, Benson Road, Forest Hill, S.E. 23. British. Superintending Chemist, Government Chemist's Department. Superintending Chemist in the Government Laboratories. Fellow of the Institute of Chemistry. (*Signed by*) Robert Robertson, Geo. Stubbs, A. More, J. J. Fox.

Hanson, Donald, 7, Willow Bank, Halifax. English. Works Chemist. Passed in Physics as subsidiary to taking Honours B.Sc. (External) of London University. Also 8 years' Laboratory and Technical Experience in Explosive Manufacture, Tar Distillation, Textile Chemistry, and Analytical Work. (*Signed by*) W. Sowden, G. C. Riley, W. J. Stansfield.

Haworth, Thomas, 8, Park Terrace, Fielding Lane, Oswaldtwistle, Lancs. English. Assistant Gas Engineer and Manager, Oswaldtwistle Urban District Council. (*Signed by*) G. W. F. Holroyd, Harry G. Leigh, J. T. Holden.

Heaton, John Stanley, 43, Birch Rd., Crumpsall, Manchester. British. Research Chemist. Student and research worker at Liverpool University for five years. B.Sc. (1st Hons.). Ph.D. Now engaged on research in textile industry. "The Investigation of Meso-thioanthracene Derivatives. Part I," Heilbron and Heaton, *J.C.S.*, 1923, **123**, 173. (*Signed by*) I. M. Heilbron, William Doran, F. C. Guthrie.

Hensman, John Cyril, M.A., A.I.C., Aldenham School, Elstree, Herts. British. Chemistry Master, Aldenham School. 1921, Cambridge Natural Sciences Tripos, Part I (Chem., Physics, Physiology); 1923, Cambridge Natural Sciences Tripos, Part II (Chemistry); 1923, elected to an Associateship of the Institute of Chemistry; 1923–4, Asst. Science Master, Rotherham Grammar School, Yorks.; 1924, Chemistry Master, Aldenham School. (*Signed by*) T. M. Lowry, W. H. Mills, Charles T. Heycock.

Hill, Joseph, 58, Spring St., Accrington, Lancs. English. Chemist (Works). Past Blackburn Tech. College, 4th year Day Course. Occupation: Chemist, East Lancashire Soap Works. (*Signed by*) G. W. F. Holroyd, Harry G. Leigh, J. T. Holden.

Hocking, Frederick Denison Maurice, 18, Woodside Park Road, N. Finchley, N. 12. British. Biochemist (and at present Final Year Medical Student, Univ. of London). M.Sc. (Lond.) with mark of distinction. A.I.C. (1920). A.C.G.F.C. and Streathfield Memorial Prize, 1919. (*Signed by*) A. Prideaux Dawson, Arthur J. Hale, H. M. Atkinson.

Hoyle, Jim, 11, Crow Lane, Ramsbottom. British. Finisher (Woollen). 2nd and 3rd Year Certificates Chemistry gained at Blackburn Technical College. 1st, 2nd, 3rd, and 4th Year Chemical Trades Course. U.L.C.I., with distinction in Magnetism and Electricity. (*Signed by*) G. W. F. Holroyd, Harry G. Leigh, J. T. Holden.

Hughes, Horace William, 27, Ombersley Rd., Balsall Heath, Birmingham. British. Schoolmaster. B.Sc. (Birmingham), Class 1 (1921). Principal Subjects: Metallurgy, Chemistry; Subsidiary: Strength of Materials. (*Signed by*) Harold Harris, Thomas Turner, Wm. Wardlaw.

Jackson, Joseph Taylor, B.Sc. (Lond.), 192, Algernon Road, Lewisham, S.E. 13. British. Lecturer in Applied Chemistry at The Leathersellers' Company's Technical College, S.E. 1. Bachelor of Science, London University. Fellow Royal Microscopical Society, London. War service (France and Salonika), Sept. 1914–Jan. 1919. (*Signed by*) Arthur Harden, Charles Dorée, S. Judd Lewis.

Jehu, David Bret, 34, High Street, Welshpool, Montgomeryshire. British (Welsh). Research Student. B.Sc., University of Wales, First Class Honours. M.Sc., University of Wales. Associate of the Institute of Chemistry. Paper

Jehu and Hudleston, *Trans.*, 1924, **125**, 1451. (*Signed by*) T. Campbell James, C. R. Bury, L. J. Hudleston, H. Medwyn Roberts.

Jobson, William, 52, The Mall, Swindon, Wilts. British. Analytical Chemist. Asst. Analyst in G. W. Rly. Chemical Laboratory, Swindon, for the last 25 years (less 4½ years' war service), appointed Chief Assistant, May 1922. Board of Education, S. and A. Dept., Inorganic Chemistry (Practical), Honours Part 1, 1903, Pass. (*Signed by*) W. R. Bird, T. C. Davison, T. Hartley.

Jones, Clifford Merton, Buxton Crescent, Newton Hill, Leeds Rd., Wakefield. British. University Student (post graduate). Science student at Queen Elizabeth's Grammar School, Wakefield (1914–1920). Laboratory assistant for two years (part time). Student in Science at University of Leeds, 1921 onwards. 2nd Class Honours B.Sc. in Chemistry, July 1924. (*Signed by*) J. B. Cohen, W. Lowson, W. A. Wightman.

Jones, Thomas William, 36, St. Vincent Road, Westcliff-on-Sea. English. Technical Chemist. B.Sc. (Hons. Chem.), London 1922. (*Signed by*) J. R. Partington, E. E. Turner, Stephen Miall, W. G. Shilling, F. A. Williams.

Keane, John, 6, Shamrock Villas, Drumcondra, Dublin. Irish. Assistant Lecturer in Chemistry, University College, Dublin. B.Sc. (First Hons.), 1917. M.Sc. 1918. Ph.D. 1922 (National University). (*Signed by*) A. G. G. Leonard, A. O'Farrelly, Sydney Young.

Lucy, Alfred, 16, Chesney Street, Battersea, London, S.W. 11. British. Junior Assistant Chemist. Twelve years' Practical Chemical experience in Works and Research Laboratories (*i.e.*, The Gas Lighting Improvement Co., Ltd.), etc. Chemistry student, attended classes up to and including the B.Sc. Standard in Theoretical and Practical Inorganic and Organic Chemistry. Battersea Polytechnic certificates for Inorganic Chemistry and Oils, Fats, and Waxes. (*Signed by*) William A. Godby, J. L. White, John Wilson.

Mabbott, Ernest Edward, 358, Fore Street, Edmonton, N. 9. British. Student. B.Sc. Engaged upon Organic Research work at East London College. (*Signed by*) J. R. Partington, E. E. Turner, A. T. Healey.

McDowall, David, 2, Kennishead Road, Thornliebank, Glasgow. British. Process Supervisor, Calico Printers, Ltd., 8 years, Manager, McDowall, Morrison & Co., Ltd., Chemical Manufacturers, and interested in research on behalf of Chemical Industry and in connection with Manufacturing Chemistry. (*Signed by*) Robert Craig McDowall, W. McHutchison, Andrew S. Matchett.

Manske, Richard H. F., The University, Manchester. British. Research Student in Chemistry, Victoria University, Manchester. B.Sc. 1923. M.Sc. 1924. Queen's University, Kingston, Canada. 1851 Exhibition Scholar, 1924—from Canada. (*Signed by*) Arthur Lapworth, R. Robinson, J. Kalff.

Moir, Hugh Clouston, 7, Craigielea St., Dennistoun, Glasgow. British. Chemist. Bachelor of Science (Applied Chemistry), Glasgow University. Associate of the Institute of Chemistry. Presently employed as Chemist by Wm. Beattie, Ltd., Dennistoun Bakery, 116, Paton St., Glasgow. (*Signed by*) G. G. Henderson, T. S. Patterson, S. Horwood Tucker.

Morton, Richard Alan, 2, Lumley Street, Garston, Liverpool. British. University Lecturer (Inorganic Chemistry). B.Sc., Ph.D. (Liv.), A.I.C. Several papers, *J.C.S.*, *Jour. Phys. Chem.* (*Signed by*) E. C. C. Baly, Harold Rogerson, I. M. Heilbron.

Moulds, Frederick Wilson, Hill Crest, Villa Road, Nottingham. British. Chemist and Druggist. Member of the Pharmaceutical Society. Chemist

in charge of the Laboratories of Messrs. Newball & Mason, Ltd., Nottingham, and a director of the firm. Late student of the University College, Nottingham, where I studied Chemistry and Pharmacy, also Industrial Bacteriology. (*Signed by*) F. S. Kipping, J. B. Firth, F. C. Laxton, Wm. H. Sims.

Myles, Andrew Joseph, 12, Gardner Rd., Tue Brook, Liverpool. British. Works Manager and Chemist. 20 Years' experience in Tar Distillation and research work on Roads Compositions. Have written and read papers on treatment of and construction of modern road surfaces. Designed a viscometer for tar and bituminous compositions. (*Signed by*) George Tate, George S. Irvine, Thomas J. Roberts.

Nash, Alfred William, 18, Prospect Rd., Moseley, Birmingham. British. Professor of Oil Engineering and Refining. B.Sc. degree for original researches on the "Pyrogenesis of Hydrocarbons." "The Berginisation of Coal and Oil," author, *Journ. Inst. Pet. Technologists*, Vol. **10**, 43. "Fuel Oil Resources of the Future," joint author, *Journ. Inst. Pet. Tech.*, Vol. **10**, 47. "Somerset Oil-shales," joint author, *Journ. Inst. Pet. Tech.*, Vol. **10**, 47. 1907–22, engaged in Oil Refineries—eventually General Manager. 1922–present, Birmingham University, Senior Lecturer, afterwards Professor. (*Signed by*) G. T. Morgan, A. E. Dunstan, Harold Harris.

Oakley, Henry Bowen, Wellcome Tropical Research Laboratories, Khartoum, Sudan. British. Assistant Government Research Chemist. Diploma of Imperial College. M.Sc. London. A.R.C.S. London. In conjunction with Prof. J. C. Philip, *J.C.S.*, 1924, **123**, 1189. (*Signed by*) A. F. Joseph, James C. Philip, M. B. Donald.

Palmer, Edgar Kent, Rose Bank, Victoria Rd., Hale, Altrincham. British. Post-graduate research. Oct. 1919–July 1923, Student at College of Technology, Manchester, in full-time degree course in the Chemical Technology of Textiles. July 1923, Grad. B.Sc.Tech. June 1924, Research under Prof. E. Knecht, Ph.D., and at present the same. (*Signed by*) Frank Lee Pyman, Edmund Knecht, John K. Wood.

Pomerantz, David, 15, Nottingham Place, Commercial Rd., E. 1. British. Student. Inter B.Sc. Two years at Royal College of Science for the 3 years necessary for the associateship (Chemistry). Am now doing the honours course at West Ham M. C. (*Signed by*) H. Bogdanor, George Dean, R. S. Glennie.

Rawlings, Harry, 15, Station Road, Ramsey, Huntingdon. British. Science master (Chemistry). B.Sc. Lond., 2nd Hons. Chemistry, 1921. Assistant Analyst, Messrs. Boots Pure Drug Co., Ltd., 1915–17. Unpublished research on organic derivs. of tin, under Prof. Kipping at Univ. Coll., Nottingham, 1921 and early 1922. Chemistry student at Univ. Coll., Nottingham, 1917 and 1919–22. Am at present working for M.Sc. (Lond.) [May 1925], and desire access to the Library of the Society. (*Signed by*) F. S. Kipping, E. B. R. Prideaux, J. B. Firth.

Reed, John Brent, 49, St. Mildred's Rd., London, S.E. 12. British. Assistant Research Chemist in the Research Laboratories of the South Metropolitan Gas Coy. Bachelor of Science, London. Associate of the Institute of Chemistry of Gt. Britain and Ireland. Student at Birkbeck College for the degree of Doctor of Philosophy. (*Signed by*) George Senter, S. Sugden, Walter T. J. Morgan, S. Medsforth.

Rhodes, William George, Park View, 318, Granville Rd. Park, Sheffield. English. Senior Science Master, Firth Park Secondary School, Sheffield. (*Signed by*) C. K. Ingold, John Evans, A. S. Russell.

Robertson, George James, M.A., B.Sc., Ph.D., The Manse, Strathkinness,

St. Andrews, Fife. British. Assistant in Chemistry and Carnegie Teaching Fellow in the University of St. Andrews. A thesis entitled "Investigations on Cellulose." Conjoint paper read by Principal Irvine before the American Chemical Society. (*Signed by*) J. C. Irvine, John Read, G. M'Owan.

Salmon, Robert Joseph, C.M.S. Medical Training College, Hangchow, Chekiang, China. British. Lecturer in Chemistry, Medical Training College, Hangchow. M.Sc. Manchester. (*Signed by*) Arthur Lapworth, Frederick Challenger, John F. Wilkinson, Harold Mastin, D. H. Bangham, Fred Fairbrother.

Shepherd, John Robert, Lady Hall Farm, Broughton-in-Furness, Lancs. British. Chemist. M.Sc. (London) in Chemistry. A.I.C. (*Signed by*) Robert H. Pickard, J. Kenyon, J. L. White, A. Houssa, Harold Hunter.

Singh, Terrain, alias Prem Chandra Sharma, Engineering College Hostel, Benares Hindu University. Indian. M.Sc. Demonstrator in the Department of Industrial Chemistry of B.H.U. M.Sc. of the Benares Hindu University with a thesis on "The Effect of the Size of the Soil-particles and Electrolytes on the Equilibrium of Moisture between the Seed and the Soil." (*Signed by*) Phuldeo Sahay Varma, S. S. Bhatnagar, N. R. Dhar.

Smith, Alan Lawrence, Bank House, 22, Dean St., Blackpool. British. *Trans. Chem. Soc.*, 1923, **123**, 1046–1055, "The Interaction of Hydrogen Sulphide, Thiocyanogen and Thiocyanic Acid on Unsaturated Compounds." M.Sc., Victoria University. (*Signed by*) Henry Stephens, Frederick Challenger, F. P. Burt, D. H. Bangham, Fred Fairbrother, John F. Wilkinson.

Thorn, George, Grove House, Beechen Grove, Watford. British. Science Master, Boys' County School, Harrow. B.Sc. (Bristol). (*Signed by*) F. Francis, J. W. McBain, F. W. Rixon.

Townsend, Leonard William Ernest, 35, Harewood Rd., Collier's Wood, Merton, S.W. 19. British. Assistant Chemist at the South Metropolitan Gas Co., 709, Old Kent Rd., S.E. Student, five years' laboratory training. (*Signed by*) S. Medsforth, E. de Barry Barnett, P. C. L. Thorne.

Walker, Leslie John, 45, Devereux Road, Wandsworth Common, S.W. 18. British. Student at the School of Pharmacy of the Pharmaceutical Society of Gt. Britain, 17, Bloomsbury Sq., W.C. 1. Pharmacist, have passed Qualifying Exam. of Pharmaceutical Society of Gt. Britain. Chemistry is included in this Exam., and it is my intention to continue studies in same. At present studying for Major Exam. of Pharmaceutical Society. (*Signed by*) C. E. Corfield, F. Browne, F. H. Lowe.

Walker, Thomas Kennedy, 4, Swythamley Road, Cheadle Heath, Stockport. British. Research Chemist to the Institute of Brewing, Research Scheme Committee. Degrees: M.Sc., Ph.D., Victoria University of Manchester. Fellow of the Institute of Chemistry. Two years' research for the Admiralty, and for two years as Assistant Chemist to Sir R. Robertson, F.R.S., in the Research Department, Royal Arsenal, Woolwich. Three years' research in Organic Chemistry with Professor A. Lapworth, F.R.S., at Manchester University. For the past three years I have been assisting Professor F. L. Pyman, F.R.S., in investigations on the preservative principles of hops under the Institute of Brewing Research Scheme. Publications: "Preparation of Sodium Ethoxide from Caustic Soda" (*Journ. Soc. Chem. Ind.*, 1921, **40**, 172T); "Condensation of Aryldiazonium Salts with Monoalkylated Malonic Acids" (*J.*, 1923, **123**, 2775); "Condensation of Aryldiazonium Salts and of Alkyl Nitrites with Cyanoacetic Acid Derivatives" (*J.*, 1924, **125**, 1622); five other papers dealing with the antiseptics of hops, of which one was published jointly with Professor Pyman and Harold Roger-

son, Esq. (*Journ. Inst. Brew.*, 1922, **19**, 929; 1923, **20**, 373; 1924, **21**, 570, 712). (*Signed by*) Frank Lee Pyman, Fredk. M. Rowe, Jas. Grant.

Waters, William Alexander, 35, Shirley Road, Cardiff. British. Research Student in Chemistry (Resident B.A. of Gonville and Caius College, Cambridge). Cambridge Natural Sciences Tripos, Part I, Class I, Cambridge Natural Sciences Tripos, Part II (Chemistry), Class I. Shuttleworth Research Studentship in Chemistry at Caius College, Cambridge. (*Signed by*) Hamilton McCombie, Harold A. Scarborough, Eric K. Rideal.

Watson, James Bernard, 30, Mulgrave Road, West Hartlepool. British. Metallurgical Chemist. Four years in the laboratory of the Technical College, West Hartlepool. Seven years as chemist in the Chemical and Metallurgical laboratory of the Central Marine Engine Works, West Hartlepool. (*Signed by*) J. W. Patterson, Gilbert Palmer, D. Arthur Ruell.

Watts, Ernest Swann, "Eaglesfield," Limefield Road, Kersal, Manchester. British. Chief Chemist, E. Griffiths Hughes, Ltd., Manchester. Qualifying Examination of the Pharmaceutical Society of Great Britain. (*Signed by*) S. Ernest Melling, Harry Brindle, Chas. Turner.

Whamond, Archibald Steele, 22, Church St., Alloa, Clackmannanshire. British. Analytical Chemist. Studied Chemistry at Heriot Watt College, Edinburgh, Day and Evening Classes, 1911–1914. March 1914–Nov. 1923, Assistant Chemist, Messrs. Wm. McEwan & Co., Ltd., Edinburgh (Army Service, Sept. 1914–Jan. 1919). Nov. 1923–present time, Chief Chemist, Messrs. Geo. Younger & Son, Ltd., Alloa. (*Signed by*) John M. Guthrie, A. Scott Dodd, John Doull.

Woodcock, Edwin John, "Stonecot," Claremont Hill, Jersey, C.I. British. Assistant Official Analyst. For the past 28 years Assistant to F. W. Toms, Esq., F.I.C., Official Analyst of Jersey, namely, the first five years as private assistant and since then as senior assistant analyst to the States of Jersey. (*Signed by*) F. W. Toms, Bernard Dyer, Alex. K. Miller, F. G. P. Remfry, G. Neville Huntly, R. Le Rossignol.

Worthington, John Stanley, 27, Rowena St., Great Lever, Bolton. British. Works Chemist. Experience in manufacture of Heavy Chemicals at Messrs. John Smith Junr. & Co., Ltd., Great Lever Chemical Works, Bolton, since 1908. Student in Advanced Chemical Tech. at Manchester College of Technology. At present have control of large Sulphuric Acid Plant. (*Signed by*) Arthur Worthington, Frank Lee Pyman, T. Trevor Potts.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2):

Bell, James Munsie, Dept. of Chemistry, Univ. of North Carolina, Chapel Hill, N.C., U.S.A. Canadian. Professor of Chemistry. Head of Chemical Department, University of N. Carolina. Formerly in Bureau of Mines, Washington, D.C., U.S.A. Numerous original publications, chiefly in the *Journal of the American Chemical Society*. (*Signed by*) James W. McBain.

Cameron, John, Peking Union Medical College, Peking, Chihli, North China. British (Scotch). Pharmacist to the above-named institution. Member of the Pharmaceutical Society of Great Britain. Publications as per attached list to date (17 articles). Instructor in Pharmacy in British Army in France, 1917–18. Lecturer in Pharmacy and Materia Medica in Peking Union Medical College, 1920–25. (*Signed by*) A. E. Newland.

McIntyre, Gordon, Sarnia, Ontario, Canada. Canadian. Chemist and Petroleum Technologist. Graduate McGill University, B.Sc., Ch.E. Chief

Chemist, Imperial Oil Refineries, Limited. (*Signed by*) Alfred Stansfield, Harold J. Roast.

Thomas, Professor Karl, M.D., Leipzig, Liebig str. 16. German. Professor ordinar. für physiologische Chemie an der Universität, Leipzig, seit 1921. Mitarbeiter von Hoppe-Seylers Zeitschrift für physiologische Chemie (herausgegeben v. Kossel) und der Biochemischen Zeitschrift (herausgegeben von Neuberg). Schüler von W. Wislicenus, H. Thierfelder und Max Rubner, Mitglied der Biochemical Society. (*Signed by*) George Barger, Robert Robinson.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Duparc, Louis, and Basadonna, M. Manuel théorique et pratique d'analyse volumétrique. 2nd edition. By Louis Duparc and Paul Wenger. Paris 1925. pp. 214. ill. 18 *fr.* (*Recd.* 18/3/25.) From the Publisher : M. Payot.

Franzen, Hans. Margarine. (Chem. Tech. in Einzeldarstellungen.) Leipzig 1925. pp. viii + 100. ill. *Gm.* 10. (*Recd.* 31/3/25.) From the Publisher : Herr Otto Spamer.

Industrial Chemist and chemical manufacturer : a journal devoted to the progress of applied chemistry and chemical engineering. Vol. I, etc. London 1925 +. (*Reference.*)
From the Publishers : The St. Margaret's Technical Press.

Königlich Preussischen Akademie der Wissenschaften zu Berlin. Monatsberichte 1876 & 1881. Berlin 1877 & 1882. (*Reference.*) From the Royal Society.

Lunge, George. The manufacture of acids and alkalis. Completely revised and rewritten under the editorship of Alexander Charles Cumming. Vol. IV. The manufacture of sulphuric acid (contact process). By Frank Douglas Miles. London 1925. pp. xvi + 428. ill. 36*s.* net. (*Reference.*)
From the Publishers : Messrs. Gurney & Jackson.

Royal Technical College, [Glasgow]. Journal : being a record of some of the research work carried out in the College by the staff and senior students. No. 1. Glasgow 1924. pp. 138. ill. (*Reference.*) From the Director.

Thorpe, Jocelyn Field, and Whiteley, Martha Annie. A student's manual of organic chemical analysis, qualitative and quantitative. London 1925. pp. x + 250. ill. 9*s.* net. (*Recd.* 19/3/25.) From the Authors.

II. *By Purchase.*

American Engineering Council. Industrial coal : purchase, delivery, and storage. New York 1924. pp. x + 420. ill. 21*s.* net. (*Recd.* 17/3/25.)

Andés, Louis Edgar. Vegetable fats and oils : their practical

preparation, purification, properties, adulteration, and examination. 4th revised and enlarged English edition. By Herbert Birtwhistle Stocks. London 1925. pp. viii + 413. ill. 15*s*. net. (*Recd*. 17/3/25.)

Back, E., and Landé, A. Zeemaneffekt und Multiplettstruktur der Spektrallinien. (Struktur der Materie in Einzeldarstellungen.) Berlin 1925. pp. xii + 214. ill. *M*. 14·40. (*Recd*. 8/4/25.)

Bassett, Henry. The theory of quantitative analysis and its practical application. London 1925. pp. x + 308. 15*s*. net. (*Recd*. 25/3/25.)

Blake, Ernest G. The seasoning and preservation of timber. London 1924. pp. xiv + 132. ill. 9*s*. 6*d*. net. (*Recd*. 17/3/25.)

Bohr, Niels. The theory of spectra and atomic constitution. 2nd edition. Cambridge 1924. pp. x + 138. ill. 7*s*. 6*d*. net. (*Recd*. 25/3/25.)

Born, Max, assisted by Friedrich Hund. Vorlesungen über Atommechanik. Vol. I. (Struktur der Materie in Einzeldarstellungen.) Berlin 1925. pp. x + 358. *M*. 15. (*Recd*. 8/4/25.)

Cohen, Julius Berend. Practical organic chemistry. 3rd edition. London 1924. pp. xvi + 520. ill. 6*s*. 6*d*. net. (*Recd*. 25/3/25.)

Field, Samuel, and Bonney, Samuel Robert. The chemical coloring of metals and allied processes. London 1925. pp. xx + 264. ill. 10*s*. 6*d*. net. (*Recd*. 25/3/25.)

Fitger, Peter. Racemisierungserscheinungen bei optisch-aktiven Sulfidsäuren. Lund 1924. pp. 134. *M*. 4. (*Recd*. 31/3/25.)

Fourneau, Ernest. Organic medicaments and their preparation. Authorised translation by William Arthur Silvester. London 1925. pp. x + 262. ill. 15*s*. net. (*Recd*. 17/3/25.)

Gooch, Frank Austin, and Browning, Philip Embury. Outlines of qualitative chemical analysis. 5th edition. New York 1924. pp. viii + 184. ill. 7*s*. 6*d*. net. (*Recd*. 25/3/25.)

Hodkin, Frederick William, and Cousen, Arnold. A textbook of glass technology. London 1925. pp. xxiv + 552. ill. 42*s*. net. (*Recd*. 17/3/25.)

Hofman, Heinrich Oscar. Metallurgy of copper. 2nd edition. Revised by Carle R. Hayward. New York 1924. pp. xiv + 420. ill. 25*s*. net. (*Recd*. 25/3/25.)

Lambert, Thomas. Bone products and manures : a treatise on the manufacture of fat, glue, animal charcoal, size, gelatin, and manures. 3rd edition, revised and enlarged by Herbert Birtwhistle Stocks. London 1925. pp. viii + 284. ill. 10*s*. 6*d*. net. (*Recd*. 25/3/25.)

Loeb, Jacques. Regeneration from a physico-chemical viewpoint. New York 1924. pp. xii + 144. ill. 10*s*. net. (*Recd* 17/3/25.)

Lucas, Alfred. Antiques : their restoration and preservation. London 1924. pp. viii + 136. 6*s*. net. (*Recd*. 25/3/25.)

Nugey, A. L. Oil refinery specifications. Easton, Pa. 1924. pp. x + 210. ill. 25*s*. net. (*Recd*. 17/3/25.)

Partington, James Riddick. A text-book of inorganic chemistry for university students. 2nd edition. London 1925. pp. xii + 1068. ill. 25*s*. net. (*Recd*. 25/3/25.)

Pulsifer, H. B. Structural metallography : an illustrated text with laboratory directions for students. Easton, Pa. 1924. pp. viii + 210. ill. 17*s*. 6*d*. net. (*Recd*. 17/3/25.)

Rector, Thomas M. Scientific preservation of food. New York 1925. pp. xii + 214. 10*s*. net. (*Recd*. 17/3/25.)

Reid, Ebenezer Emmet. Introduction to organic research. [New York 1924.] pp. viii + 344. 24*s*. net. (*Recd*. 6/4/25.)

Rinne, Friedrich. Crystals and the fine-structure of matter. Translated by Walter S. Stiles. London 1924. pp. x + 196. ill. 10*s*. 6*d*. net. (*Recd*. 17/3/25.)

Stillman, John Maxson. The story of early chemistry. New York 1924. pp. xiv + 566. 18*s*. net. (*Recd*. 25/3/25.)

Thresh, John Clough, and Beale, John Foster. The examination of waters and water supplies. 3rd edition. London 1925. pp. xiv + 590. ill. 25*s*. net. (*Recd*. 17/3/25.)

III. *Pamphlets.*

Board of Agriculture and Fisheries. Statutory rules and orders, 1908, No. 964. Adulterations. Fertilisers and feeding stuffs. The fertilisers and feeding stuffs (methods of analysis) regulations, 1908. London 1908. pp. 9.

Grün, Richard. Die Einwirkung des Sulfidgehaltes auf die Eigenschaften von Hochofenschlacken und Hüttenzementen. (From *Stahl und Eisen*, 1925, **45**.)

Harold, Charles Henry Hasler, and Ward, Arthur Rokeby. Report on experimental work carried out at the Army School of Hygiene to demonstrate that chlorine gas in association with ammonia gas is a more efficient sterilizer of water than chlorine gas used alone or chloros or bleaching powder. (From the *J. Roy. Army Med. Corps*, 1924, **41**.)

Joseph, Alfred Francis, Martin, Frederick John, and Hancock, J. S. The electrical method for determining soil alkali. (From the *Cairo Sci. J.*, 1924, **12**.)

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, May 7th, 1925, at 8 p.m., Professor J. C. PHILIP, O.B.E., D.Sc., F.R.S., Vice-President, in the Chair.

The CHAIRMAN referred to the loss sustained by the Society, through death, of the following Fellows :

	Elected.	Died.
Edward Wightman Bell	June 20th, 1889.	Jan. 29th.
Arthur Boake	Dec. 2nd, 1875.	April 12th.
William Dugdale Harland	Feb. 7th, 1878.	April 23rd.
Sir David L. Salomons	May 4th, 1876.	April 19th.
George Young	Dec. 4th, 1890.	April 3rd.

The CHAIRMAN announced :

1. That the following address of congratulation had been sealed and would be presented to the Royal University of Pavia on the occasion of the Centenary Celebrations of that University which were being held from May 20th to 22nd, 1925 :

To the Rector, Senate, Professors, and Alumni of the Royal University of Pavia from The Chemical Society.

The Chemical Society sends cordial greetings and felicitations to the illustrious University of Pavia on the completion of no less than eleven centuries of high service to mankind.

As representatives of a Science rooted in antiquity, we gratefully acknowledge the debt we owe to the members of your University who throughout the ages preserved ancient learning and extended the boundaries of knowledge, giving to us our heritage. We do not forget that the celebrated Lanfranc, one of your earliest and greatest teachers, carried the torch of learning to our country as Archbishop of Canterbury. Since her foundation the University of Pavia has given to the world many men distinguished for learning

and science—Alexander Volta, who pointed out new paths which now we follow, Camillus Golgi, the great neurologist, and many others whose genius we gratefully acknowledge.

We join with those who will be hastening from all parts of the world to lay before you their tribute of praise, and we hope that in the future renewed prosperity will be added to your illustrious past.

Signed on behalf of the Chemical Society.

ARTHUR W. CROSSLEY, *President.*
JOCELYN THORPE, *Treasurer.*
T. SLATER PRICE, } *Secretaries.*
C. S. GIBSON, }
F. G. DONNAN, *Foreign Secretary.*

(L.S.)

Sealed this Seventh day of May, One Thousand Nine Hundred and Twenty Five.

2. That a copy of the works of the late Walthère Spring had been presented to the Library by the Belgian Chemical Society, and that this volume can be purchased from Monsieur J. Wauters, Secrétaire, Société Chimique de Belgique, 83, Rue Souveraine, Brussels, price 40 francs, post free.

The following were formally admitted Fellows of the Chemical Society: Alan D. Whitehead, Stuart R. Parsons, Leslie S. Theobald, J. F. J. Rule, and A. H. B. Bishop.

Certificates were read for the first time in favour of:

Maung Hla Baw, R-1, 64th Street, Danneedaw, Rangoon.
Joseph John Blackie, c/o Messrs. Duncan, Flockhart & Co., 104, Holyrood Road, Edinburgh.
Samuel Cyril Blacktin, M.Sc., 173, Ecclesall Road South, Sheffield.
Nirmal Boran Brohmachary, B.Sc., Ghugudanga-Post, 24, Porganas, Calcutta.
Gertrude Margaret Bullick, B.Sc., 43, Belsize Park, Hampstead, N.W. 3.
Ralph Edgar Cable, Queen's Gardens, Hong Kong.
Leslie Marshall Clark, B.A., Ph.D., A.I.C., 38, Park Road, Hampton Wick.
Clive Kear Colwell, B.A., Ormesty, Great North Road, N. 2.
Jan Coops, 25, Sireelinckplein, The Hague, Holland.
William George Corderoy, B.Sc., 35, Century Road, Walthamstow, E. 17.
Oswald Pilkington Cronshaw, 141, Blackburn Road, Great Harwood, Blackburn.
John Alexander Currie, B.A., B.Sc., 44, Phillimore Gardens, W. 8.
Thomas Dillon, University College, Galway.
Octave Charles Marie Dony, 30, Rue Émile Banning, Brussels.
William Edward Gibbs, D.Sc., 4, Stanley Villas, Runcorn.
Ernest Hartshorne, B.Sc.Tech., 12, Muriel Street, Broughton.
Arthur Harvey, 12, Chaldon Road, Fulham, S.W. 6.
Charles Richard Hennings, Ph.D., 19, St. Dunstan's Hill, E.C. 3.
Noel Waterman Vere Jones, Eastnook, Pakefield, Lowestoft.
Frank William Linch, M.Sc., F.I.C., 89, Hazelbottom Road, Cheetham, Manchester.

Charles Lipshaw, 48, Lower Broughton Road, Salford.
James Arthur Prescott, The University, Adelaide.
Malik Karam Singh, B.Sc., Rawalpindi City, India.
Norman Heath Smith, B.Sc., Anglo-Persian Oil Co., Ltd., Abadan.
John Thurgood, B.Sc., Roseleigh, Elmwood Avenue, Harrow.
Shojiro Uchida, 12, Shinryudo-Machi, Azabu-Ku, Tokio.
John Henry Walker, A.I.C., Gourepore Works, Naihati, E.B.Ry., Bengal.

Messrs. H. Burton and J. N. Sugden were elected Scrutators, and a ballot for the election of Fellows was held, the following subsequently being declared elected as Fellows :

James Munsie Bell.
Niels Janniksen Bjerrum.
Archibald Beresford Blunsden.
Geoffrey Alger Blyde.
Thomas Henry Bowles.
William Harrison Brindley, M.C., M.A., M.Sc.Tech., A.I.C.
James Lindsay Buchan, B.Sc.
Frank Henry Charles Bull, B.Sc., A.I.C.
John Alfred Valentine Butler, M.Sc.
Annie Lavinia Byford, B.Sc.
John Cameron.
James Herbert Clegg.
Horace Cecil Cockroft, B.Sc., A.I.C.
Francis Xavier Coyne.
James Craik, M.A., B.Sc., Ph.D.
Herbert Greetham Dane, M.Sc.
Harry Dean.
Margaret Stedman Leonora Dixon.
Robin George Westbury Farnell, A.R.C.S., A.I.C.
Irvine John Faulkner.
Thomas Flett, B.Sc., A.I.C.
Thomas James Elijah Gardner.
Richard Randolph Garran, B.Sc.
John Charles Giblin, B.Sc., A.I.C.
Helen Simpson Gilchrist, B.Sc., Ph.D.
Isabel Hodgson Hadfield, M.Sc.
James Francis Halpin, F.I.C.
Donald Hanson.
Thomas Haworth.
John Stanley Heaton, B.Sc., Ph.D.
John Cyril Hensman, M.A., A.I.C.
Joseph Hill.
Frederick Denison Maurice Hocking, M.Sc., A.I.C.
Jim Hoyle.
Horace William Hughes, B.Sc.
Joseph Taylor Jackson, B.Sc.
David Bret Jehu, M.Sc., A.I.C.
William Jobson.
Clifford Merton Jones, B.Sc.
Thomas William Jones, B.Sc.
John Keane, M.Sc., Ph.D.
Alfred Lucy.
Ernest Edward Mabbott, B.Sc.
David McDowall.
Gordon McIntyre, B.Sc., Ch.E.
Richard H. F. Manske, M.Sc.
Hugh Clouston Moir, B.Sc., A.I.C.
Richard Alan Morton, B.Sc., Ph.D., A.I.C.
Frederick Wilson Moulds.
Andrew Joseph Myles.
Alfred William Nash, B.Sc.
Henry Bowen Oakley, M.Sc., A.R.C.S.
Edgar Kent Palmer, B.Sc.Tech.
David Pomerantz.
Harry Rawlings, B.Sc.
John Brent Reed, B.Sc., A.I.C.
William George Rhodes.
George James Robertson, M.A., B.Sc., Ph.D.
Robert Joseph Salmon, M.Sc.
Prem Chandra Sharma, M.Sc.
John Robert Shepherd, M.Sc., A.I.C.
Alan Lawrence Smith, M.Sc.
Karl Thomas, M.D.
George Thorn, B.Sc.
Leonard William Ernest Townsend.
Leslie John Walker.
Thomas Kennedy Walker, M.Sc., Ph.D., F.I.C.
William Alexander Waters, B.A.
James Bernard Watson.
Ernest Swann Watts.
Archibald Steele Whamond.
Edwin John Woodcock.
John Stanley Worthington.

The following papers were read :

"The tautomerism of dyads. Part III. The effect of the triple linking on the reactivity of neighbouring atoms." By Mrs. E. H. Ingold.

"The rotatory dispersive power of organic compounds. Part XVI. Halogen-derivatives of camphor." By J. O. Cutter, H. Burgess, and T. M. Lowry.

"The isomerism of the oximes. Part XXII. The configuration of the aldoximes." By O. L. Brady and G. Bishop.

"The parachor and chemical constitution. Part I. Polar and non-polar valencies in unsaturated compounds." By S. Sugden, J. B. Read, and H. Wilkins.

"The tautomerism of dyads. Part IV. New evidence of the tautomeric mobility of oximes." By J. P. Griffiths and C. K. Ingold.

Ordinary Scientific Meeting, Thursday, May 21st, 1925, at 8 p.m., Professor W. P. Wynne, D.Sc., F.R.S., Vice-President, in the Chair.

The Chairman referred to the loss sustained by the Society, through death, of the following :

	Elected.	Died.
Albin Haller (Honorary Fellow)	Feb. 6th, 1908.	May 1st.
Samuel Henry Davies	Feb. 15th, 1894.	May 9th.
John Mylne Mullaly	May 4th, 1922.	May 4th.

It was also announced that the Celebration of the Centenary of Faraday's discovery of benzene, which is being arranged by the Royal Institution in association with the Chemical Society, the Society of Chemical Industry, and the Association of British Chemical Manufacturers, will take place at the Royal Institution on Tuesday, June 16th, 1925. In the morning, at eleven o'clock, there will be a reception by the Duke of Northumberland of English and foreign delegates, and several short addresses will be delivered commemorative of Faraday's chemical work. In the evening, a banquet will be held in the Goldsmiths' Hall, the price of the tickets being £2 2*s*. each, including wine. Application for tickets for the reception and for the banquet, which are limited in number, should be made to the Secretary, The Royal Institution, Albemarle Street, W. 1.

Mr. H. G. Dane was formally admitted a Fellow of the Chemical Society.

Certificates were read for the first time in favour of :

Marion Alice Battie, B.Sc., A.I.C., The Orchard, Ivy Lane, Woking.
William Ambler Berry, B.Sc., 19, Blakeney Road, Sheffield.

Thomas Anthony Canning, Crindau Gas Works, Newport, Mon.
John Carroll Culbert, 172, North Road, Belfast.
Alexander John Dey, F.R.S.E., Rothiemay, Corstorphine, Edinburgh.
Stanley James Featherston, 33, Belmont Road, Beckenham.
James Hindle, 4, Plane Street, Blackburn.
Thomas Moore, B.Sc., 8, Cyprus Avenue, Belfast.
Alexander John Morrison, Testing Branch, Public Works Department, Sydney, N.S.W.
Frank Richard Morrison, Brae Street, Waverley, Sydney, N.S.W.
Ernest Charles Padgham, 30, Churchill Road, N.W. 2.
John Monteath Robertson, B.Sc., A.I.C., The Chemistry Department, The University, Glasgow.
Ernest Henry Warren, B.A., 1, Chamber's Lane, Willesden Green, N.W. 10.
James Watt, F.R.S.E., Craiglockhart House, Slateford, Edinburgh.
William John Willis, Hazel Mount, Carnforth.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2) :

Howard Ecker, 1510, Dana Avenue, Cincinnati, Ohio, U.S.A.
William Beesley, Binnyston Gardens, Bangalore, India.
Alexander Smith, P.O. Box 103, Nairobi, Kenya Colony.

The following papers were read :

"The rotatory dispersion of derivatives of tartaric acid. Part II. Acetyl derivatives." By P. C. Austin and J. R. Park.

"The stability of additive compounds between esters and acids." By J. Kendall and J. E. Booge.

"Additive compounds in the ternary system, acid–ester–water." By J. Kendall and C. V. King.

"A spectroscopic study of the combustion of phosphorus trioxide and of phosphine." By H. J. Emeléus.

"The nature of the alternating effect in carbon chains. Part III. A comparative study of the directive efficiencies of oxygen and nitrogen atoms in aromatic substitution." By E. L. Holmes and C. K. Ingold.

LIST OF FELLOWS, 1925.

It has been decided to print the List of Fellows for 1925 and to supply the List to those Fellows who make application to the Assistant Secretary by the 31st July, 1925.

BERICHTE, 1915 to 1924.

Sets of the Berichte from 1915 to 1924 (10 years) are now offered to Fellows of the Society at £22, carriage extra. Application should be made to Mr. S. E. Carr.

List of Papers, or Abstracts thereof, received between April 3rd and May 21st, 1925. (This List does not include the titles of papers which have been read at a Scientific Meeting, or which have appeared in the Journal.)

"The ionisation of aromatic nitro-compounds in liquid ammonia." By M. J. Field, W. E. Garner, and C. C. Smith.

"α-Acenaphthoquinoline." By J. Stewart.

"Alcohols of the hydroaromatic and terpene series. Part IV. α- and β-Fenchyl alcohols and some esters derived therefrom." By J. Kenyon and H. E. M. Priston.

"Perkin's reaction." By T. Hopkins.

"Action of zinc alkyl halides on nitric esters." By T. Hopkins.

"Polynuclear heterocyclic aromatic types. Part II. Some anhydronium bases." By J. W. Armit and R. Robinson.

"β-Piperonylpropionitrile and some derived substances." By W. Baker and R. Robinson.

"The melting points of benzene derivatives." By T. Beacall.

"Nitrosation of phenols. Part II. 3-Bromo-, 2-bromo-, 3-iodo-, and 2-iodo-phenols, with evidence favouring the nitroso form for 4-nitroso phenol." By H. H. Hodgson and F. H. Moore.

"The Kekulé formula for benzene and the existence of isomeric ortho disubstitution products." By H. H. Hodgson and J. H. Wilson.

"A new method of diagnosing potential optical activity. Part I. The optical activity of chlorobromomethanesulphonic acid." By J. Read and A. M. McMath.

"The carboxy-phenyl camphoramic acids." By M. Singh and R. Singh.

"A simplified method of micro-combustion: the micro-Dennstedt method." By C. Funk and S. Kon.

"Interfacial tension." By J. R. Pound.

"Low temperature oxidation at charcoal surfaces. Part I. The behaviour of charcoal in the absence of promoters." By E. K. Rideal and W. M. Wright.

"Osmotic pressure by the solubility method in concentrated solutions." By M. P. Applebey and P. G. Davies.

"Synthetical experiments in the naphthyridine groups." By J. M. Gulland and R. Robinson.

"Chlorobenzothiazole dibromide." By R. F. Hunter.

"Note on the action of sodium of chlorobenzothiazole." By R. F. Hunter.

"Investigations into the analytical chemistry of tantalum, niobium, and their mineral associates. Part III. A new method for

the separation of tantalum from niobium. Part IV. The detection and determination of tantalum in niobium compounds." By A. R. Powell and W. R. Schoeller.

"The conditions underlying the formation of unsaturated and cyclic compounds from halogenated open-chain derivatives. Part VII. The influence of the phenyl group on the formation of the *cyclo*propene ring." By W. Haerdi and J. F. Thorpe.

"Rapid determination of copper and iron in mixtures of their salts." By A. S. Russell.

"The bromination of 4′-amino-1-phenyl-5-methyl benzothiazole and of 1 : 1-bisbenzothiazole." By R. F. Hunter.

"Amino benzothiazoles. Part I. 1-Phenylamino benzothiazole and its homologues." By R. F. Hunter.

"The directing influence of the methane sulphonyl group." By R. F. Twist and S. Smiles.

"The dissociation constants of selenious acid." By J. S. Willcox and E. B. R. Prideaux.

"The velocity of benzylation of certain amines. Part II." By D. H. Peacock.

"Measurements of energy absorption of certain photo-chemical reactions with iodine." By B. K. Mukerji and N. Dhar.

"The action of hydrogen peroxide on limonene." By J. Sword.

"Synthetical experiments in the *iso*quinoline group. Part I." By R. D. Haworth and W. H. Perkin.

"Synthetical experiments in the *iso*quinoline group. Part II." By R. D. Haworth, W. H. Perkin, and J. Rankin.

"Synthetical experiments in the *iso*quinoline group. Part III." By R. D. Haworth and W. H. Perkin.

"Synthetical experiments in the *iso*quinoline group. Part IV." By R. D. Haworth and W. H. Perkin.

"Synthesis of ψ-protoberberine and ψ-protopapaverine." By J. S. Buck, W. H. Perkin, and T. S. Stevens.

"Note on a laboratory method of preparing *p*-benzoquinone." By R. Craven and W. A. T. Duncan.

"Hydroxybenzils." By J. T. Marsh and H. Stephen.

"Researches on sulphuryl chloride. Part III. Influence of catalysts on the chlorination of toluene." By O. Silberrad, C. A. Silberrad, and B. Parke.

"The adsorption of water from the gas phase on plane surfaces of glass and platinum." By I. R. McHaffie and S. Lenher.

"The action of phosphorus pentachloride on 2-*iso*nitroso-1-hydrindones." By R. D. Haworth and H. S. Pink.

"Oxidation products of oleic acid. Part I. Conversion of oleic acid into dihydroxystearic acid and the determination of the

higher saturated acids in mixed acids from natural sources." By A. Lapworth and E. N. Mottram.

"The spatial structure of *cyclo*paraffins. Part I. A new aspect of Mohr's theory and the isomerism of decahydronaphthalene." By W. A. Wightman.

"The absorption spectra of the vapours of anthracene and anthraquinone, phenanthrene, and phenanthraquinone, and other quinones." By J. E. Purvis.

"Investigations on the dependence of rotatory power on chemical constitution. Part XXVII. Some esters of *p*-toluene-sulphonic and -sulphinic acids." By H. Phillips.

"Oxidations in turpentine and olive oil." By E. Walker.

"Colour and molecular geometry. Part IV. Explanation of the colours of the cyanine dyes." By J. Moir.

"The surface tensions of aqueous phenol solutions. Part II. Activity and surface tension." By A. K. Goard and E. K. Rideal.

"Triad groups in complexes of octahedral symmetry." By J. D. M. Smith.

"*Iso*quinoline derivatives. Part IX. Preparation and reduction of *iso*quinoline and its derivatives." By R. Forsyth, C. I. Kelly, and F. L. Pyman.

"The nitration of *m*-meconine." By J. N. Rây and R. Robinson.

"Chenopodium oil. Part II. The hydrocarbon fraction." By T. A. Henry and H. Paget.

"The amino-γ-pyridones." By W. H. Crowe.

"Studies of the glucosides. Part III. The synthesis of thioindican." By J. Craik and A. K. Macbeth.

"The reduction of the bromoanthraquinones." By E. de B. Barnett and J. W. Cook.

"The chlorination of acetanilide and the chloroamine-chloroanilide transformation." By F. G. Soper.

"The thermal decomposition of ozone." By R. O. Griffith and A. McKeown.

"Studies of electrolytic polarisation. Part III. The diffusion layer." By S. Glasstone.

"Theories of polar and non-polar free affinities. A practical and theoretical reply to some recent criticisms and comparisons." By G. N. Burkhardt and A. Lapworth.

"The reaction between sodium hypobromite and urea." By M. B. Donald.

"Echitamine." By J. A. Goodson and T. A. Henry.

"The preparation of phthalamic acids and their conversion into anthrenilic acids." By E. Chapman and H. Stephen.

"An *X*-ray examination of maleic and fumaric acid." By K. YARDLEY.

"The estimation of arsenic in organic compounds." By G. NEWBERY.

"The bromination of acyl derivatives of phenylhydrazine: the preparation of 2 : 4-dibromophenylhydrazine." By J. E. HUMPHRIES and R. EVANS.

"The system chromium trioxide–boric acid–water." By L. F. GILBERT.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE BALLOT TO BE HELD AT THE ORDINARY SCIENTIFIC MEETING ON THURSDAY, JUNE 18TH, 1925.

BATTIE, MARION ALICE, The Orchard, Ivy Lane, Woking, Surrey. British. Post-graduate student. B.Sc. Honours (Chemistry), Class II. Associate of the Institute of Chemistry. (*Signed by*) T. S. Moore, Mary Boyle, S. Smiles.

BAW, MAUNG HLA, R-1, 64th Street, Danneedaw, Rangoon. Burmese. Analytical Chemist, Messrs. E. M. D'Souza & Co., Rangoon, and Science Master, St. John's College, Rangoon. Passed the Intermediate Examination in Science of the Calcutta University in 1916, taking Chemistry, Physics, and Mathematics. Process Chemist (1916 to 1921) at the Seikkyi Refinery of Messrs. The Indo Burma Petroleum Co., Ltd.; and Process Chemist (1922) in the acid works of The Burma Chemical Industries, Ltd. Process Chemist (1923) with The Rangoon Pharmaceutical and Chemical Works, Rangoon. Since 1924 chemist in charge of the analytical laboratory of Messrs. E. M. D'Souza & Co., Rangoon, and Science Master, St. John's College, Rangoon. (*Signed by*) Maung Tun Tin, Maung Ba, Maung Ba San.

BERRY, WILLIAM AMBLER, 19, Blakeney Rd., Sheffield. British. Research Student at University of Sheffield. B.Sc., Hons. Chem., 1924. Joint author with Dr. G. M. Bennett of the Note, *J.C.S.*, 1925, **127**, 910. (*Signed by*) W. P. Wynne, T. M. Lowry, G. M. Bennett, F. G. Tryhorn.

BLACKIE, JOSEPH JOHN, c/o Duncan, Flockhart & Co., 104, Holyrood Road, Edinburgh. British. Pharmaceutical Chemist. Minor and Major Examination, Pharmaceutical Society of Great Britain. Laboratory Manager of Messrs. Duncan, Flockhart & Co., Manufacturing Chemists, Edinburgh. Examiner in Chemistry of the Pharmaceutical Society of Great Britain. (*Signed by*) George Barger, William Duncan, Eric Knott.

BLACKTIN, SAMUEL CYRIL, 173, Ecclesall Road South, Sheffield. British. Research Assistant. (Junior Assistant, Safety in Mines Research Laboratories, Badger Lane, Sheffield.) M.Sc. (Sheffield). (*Signed by*) W. P. Wynne, F. G. Tryhorn, J. Kenner.

BLIGH, NEVILLE MELTON, 67, Castle Road, Bedford. British. Science Master. A.R.C.S. (Chemistry), London, 1921. A.I.C., 1923. Formerly Senior Science Master, Wimborne Grammar School, Dorset. At present (Temporary) Senior Science Master, Stevenage Grammar School, Herts. *Signed by*) H. B. Baker, James C. Philip, M. A. Whiteley.

BORLAND, HUGH ALEXANDER MILLAR, 14, Cotham Road, Bristol. British.

Teacher of Chemistry. A.R.C.S. (Lond.). M.Sc. (Bristol). Lecturer on Chemistry 1896 to present date (Secondary and Technical). Lecturer on Applied Chem., University of Bristol, 1910–19. (*Signed by*) Arthur Marsden, F. Francis, J. W. McBain, F. W. Rixon.

Brohmachary, Nirmal Boran, Ghugudanga-Post 24 Porganas, Calcutta, India. Hindu (Indian). Chemist to Messrs. B. K. Paul's Chemical and Pharmaceutical Works, Dum Dum, Calcutta. Passed the B.Sc. examination of the Calcutta University in 1920. Worked as an analytical and manufacturing chemist. Assistant of Messrs. Smith, Stanistreet & Co. for 2 years, and at present working as the Chemist for Messrs. B. K. Paul & Co. (for last three years). (*Signed by*) Dhirendra Nath Mukerji, Sudhindranarayan Ray, R. L. Jenks.

Bullick, Gertrude Margaret, 43, Belsize Park, Hampstead, N.W. 3. British. Hons. Student in Chemistry, Bedford College, Univ. of London. Graduate of Lond. Univ. B.Sc., June, 1924. (*Signed by*) Holland Crompton, J. F. Spencer, M. S. Crewdson, J. Stewart.

Cable, Ralph Edgar, Queen's Gardens, Hong Kong. English. Apothecary, Medical Department, Hong Kong. Lecturer (part time), University of Hong Kong, Med. Faculty, Practical Pharmacy. (*Signed by*) R. W. E. Stickings, A. J. Ewins, G. Newbery, P. Blenkinsop.

Canning, Thomas Anthony, Crindau Gas Works, Newport, Mon. English. Gas and Chemical Engineer, now General Assistant Technical Engineer to the Newport (Mon.) Gas Company. Certificates in Chemistry granted by Institution of Gas Engineers. Engaged 7 years in Gas Manufacture and allied work and the chemistry of same. I desire to become a Fellow of the Chemical Society in order to keep in touch with current chemical literature. (*Signed by*) Geo. R. Thompson, H. E. Cox, J. H. Canning.

Clark, Leslie Marshall, 38, Park Rd., Hampton Wick, Kingston-on-Thames. English. Chemist, National Physical Laboratory, Teddington. Late Scholar and Research Scholar, Sidney Sussex College, Cambridge. Late Assistant Demonstrator, Cambridge University Chemical Laboratory. B.A., Cantab. Ph.D., London. Associate of Institute of Chemistry. Joint author of papers in *J.C.S.*, 1923, **123**, 2353, and 2362. (*Signed by*) M. Johnson, Guy Barr, Percy G. Ward.

Colwell, Clive Kear, Ormesty, Great North Road, N. 2. English. Analytical and Consulting Chemist. B.A., Cantab. Paper in conjunction with A. J. Berry, M.A., in Chemical News. (*Signed by*) A. H. M. Muter, Cyril Dickinson, J. Kear Colwell.

Coops, Jan, den Haag, 25 Sireelinckplein. Dutchman. Dr. ir. Delft. Assistant, Commercial University, Rotterdam. Author of some papers in *Rec. trav. chim.*, 1920, 1921, 1922, 1923, 1924, 1925, *Chem. Weekblad*, and *Kon. Akad. van Weten. Amsterdam*, etc. (*Signed by*) H. J. Backer, Ernest Cohen, A. Smits.

Corderoy, William George, 35, Century Rd., Walthamstow, E. 17. British. Student for Teaching Profession (entering profession next Sept.). 1st Honours (Chem.), B.Sc. (Lond.). [Studied at East London College, 1921–24.] (*Signed by*) J. R. Partington, E. E. Turner, D. C. Jones, Elwyn Roberts.

Cronshaw, Oswald Pilkington, 141, Blackburn Road, Great Harwood, near Blackburn. British. Chemist and Assistant Gas Engineer, Accrington District Gas and Water Board. For past 3 years Chief Chemist to the Accrington District Gas and Water Board, having full chemical control of all gas manufacturing operations, the manufacture of sulphate of ammonia,

etc. Hold 1st Class Certificates Gas Manufacture (City and Guilds). Distinction in Inorganic Chemistry (Lanc. and Cheshire Inst.). 1st Class Certificate Inorganic and Organic Chemistry at Blackburn College of Technology. Associate Member of Institution of Gas Engineers. (*Signed by*) James Booth, John S. Morrison, Robert C. McDowall.

Culbert, John Carroll, 172, North Road, Belfast. British. Pharmacist. Pharmaceutical Chemist, Member of Pharm. Society of Ireland, ex-Member Council of Pharm. Society of Ireland. (*Signed by*) George Scott Robertson, W. H. Gibson, Henry Wren.

Currie, John Alexander, 44, Phillimore Gardens, London, W. 8. British. Student. Honours B.A., Chemistry, and B.Sc., Oxford. Now researching under Professor Donnan at University College, London. (*Signed by*) F. G. Donnan, W. E. Garner, C. W. Bonniksen.

Dey, Alexander John, Rothiemay, Corstorphine, Edinburgh. British. Manufacturing Chemist. Managing Director, T. and H. Smith, Ltd., Manufacturing Chemists. F.R.S.E. (*Signed by*) James Walker, Alex. C. Cumming, Alexander Lauder.

Dillon, Thomas, University College, Galway. Irish. Professor of Chemistry, University College, Galway. Papers on Waxes, *Proc. R.D.S.*, 1909, vol. 12, No. 20; vol. 15, No. 10; *Proc. R.I.A.*, vol. 29, sec. B, No. 8. On separation of Isotopes of Lead, *Proc. R.D.S.*, 1922, vol. 17, p. 53. (*Signed by*) A. G. G. Leonard, Sydney Young, Emil A. Werner, A. O'Farrelly.

Dony, Octave Charles Marie, Bruxelles, 30 Rue Emile Banning. Belge. Professeur à l'Université de Bruxelles (Faculté de Science appliquées). Membre de l'Académie royale de Belgique. (*Signed by*) C. S. Gibson, Eric K. Rideal, T. M. Lowry, W. J. Pope, Henry E. Armstrong.

Featherston, Stanley James, 33, Belmont Rd., Beckenham, Kent. British. Analytical Chemist in Laboratory of Manufacturing Chemists, namely, Messrs. Hopkins & Williams, 16–17, Cross St., E.C. Honours Student in Chem. at Birkbeck Coll., University of London. 5 Years analytical work with manufacturing chemists. (*Signed by*) George Senter, F. Barrow, Samuel Sugden.

Gaskill, Malcolm Sinclair, 3, Buckingham Rd., Hilton Park, Prestwich, Manchester. British. Chemical Engineer, West's Gas Improvement Co., Ltd., Manchester. Associate of the Manchester College of Technology. Chemist and Assistant Manager, Messrs. Hardman & Holden, Ltd., Chemical Manufacturers, Clayton. Present position, as above. Desirous of keeping in touch with modern developments of pure and applied chemistry. (*Signed by*) Harold G. Colman, William Buckley, Joseph Poulson.

Gibbs, William Edward, 4, Stanley Villas, Runcorn. British. Chief Chemist to the Salt Union, Ltd. D.Sc. (Liverpool). Author of books: "Clouds and Smokes: The Properties of Disperse Systems in Gases," "The Dust Hazard in Industry." *Journ. Inst. Metals*, XV (1916), 1, pp. 41–191; *J.S.C.I.*, XLI, pp. 189–196; *Faraday Soc.*, XI, 1915, pp. 295–297, etc. (*Signed by*) W. C. McC. Lewis, I. M. Heilbron, E. C. C. Baly.

Hamer, Norman, "Ash Mount," Holcombe, nr. Manchester. British. Research and Analytical Chemist in Calico Printing, Dyeing, and Bleaching Works. As a student I have gained the Associateship of the Manchester College of Technology (Assoc. M.C.T.), whilst my duties as chemist cover a fairly wide field of analytical work, together with the investigation of the many and varied problems which are continually arising in the works. (*Signed by*) Arthur M. Morley, John K. Wood, Frank Lee Pyman.

Hartshorne, Ernest, 12, Muriel St., Broughton, Manchester. British.

Chemist in the Laboratory of Dr. A. K. Miller, F.C.S. Degree of Bachelor of Technical Science in General Chemical Technology, Victoria University, Manchester. (*Signed by*) Alex. K. Miller, Frank Lee Pyman, John K. Wood.

Harvey, Arthur, 12, Chaldon Road, Fulham, S.W. 6. British. Chemist. Formerly Agricultural Analyst, South Eastern Agricultural College (Univ. Lond.), Wye, Kent. Formerly lecturer on Applied Chemistry, Leathersellers College, London. Author of "Practical Leather Chemistry" and "Tanning Material," published by Crosby Lockwood & Son. Also several papers on leather chemistry in *J. Soc. L. Trades Chem.* Editor of Abstracts, *J. Soc. L. Trades Chem.* Member, British Association of Chemists, American Chemical Society, Society of Leather Trades Chemists. (*Signed by*) M. C. Lamb, A. B. Bradley, R. W. West.

Hennings, Charles Richard, 19, St. Dunstan's Hill, London, E.C. 3. German. Consulting Chemist. Qualified Pharmaceutical Chemist. Graduated in Chemistry. Ph.D., Freiburg. Papers as given before when first being admitted. (*Signed by*) Otto Oberländer, George P. Forrester, A. W. Edwards.

Hindle, James, 4, Plane St., Blackburn, Lancs. British. Student. Have been full-time day student in the Chemistry Dept. Municipal Technical College, Blackburn, for four years and am now preparing for Hons. Chemistry, B.Sc. (Lond.) there. (*Signed by*) G. W. F. Holroyd, Harry G. Leigh, J. T. Holden.

Jones, Noel Waterman Vere, Eastnook, Pakefield, Lowestoft. British. Student. Have been studying Chemistry for five years and wish to keep abreast of modern advances. (*Signed by*) E. de Barry Barnett, James W. Cook, Marcus A. Matthews.

Linch, Frank William, 89, Hazelbottom Rd., Cheetham, Manchester. British. Research Chemist, British Dyestuffs Corporation. M.Sc., Lond. 1st Hons. Chemistry at B.Sc. F.I.C. Asst. Chief Chemist, H.M. Factory, Queensferry, 1915–1917. Chief Chemist, H.M. Factory, Avonmouth, 1917–1919. 1919 to date, Research Chemist, British Dyestuffs Corp., Blackley, Manchester. Action of sodium hypobromite on carbamide derivs. Part I. 3-Amino-coumarin. Both papers in Trans. 1912. (*Signed by*) G. R. Clemo, Colin H. Lumsden, Anthony J. Hailwood.

Lipshaw, Charles, 48, Lr. Broughton Rd., Salford. British. Chemist to Messrs. Halliday & Co., Ltd., Bankfield Mills, Stockport. 4 years Laboratory Chemist, and Assistant Works Chemist, at Lowerhouse Printworks, Burnley. Student at the Royal Technical College, Salford. Diploma of the College, City and Guilds of London Institute, Final Certificates in Dyeing and Textile Printing. (*Signed by*) S. N. Brown, V. Edge, E. Clark, B. Prentice.

Moore, Thomas, 8, Cyprus Avenue, Belfast. British. Student. Graduate of London (with Honours) and of the Queen's University, Belfast. Fifth year research student in Photochemistry. (*Signed by*) Wm. H. McVicker, Joseph K. Marsh, A. W. Stewart, H. Graham.

Nixon, Ivor Gray, 75, The Vale, Golder's Green, N.W. 11. English. Student. Have studied chemistry for over 6 years and desire to keep abreast of modern developments. (*Signed by*) E. de Barry Barnett, P. C. L. Thorne, James W. Cook.

Occleshaw, Vincent Joseph, 22, Bryn Street, Ashton-in-Makerfield, nr. Wigan. British. Lecturer and Demonstrator in Inorganic Chemistry. M.Sc. (Liv.). A.I.C. (*Signed by*) E. C. C. Baly, J. T. Nance, A. O. Jones.

Padgham, Ernest Charles, 30, Churchill Road, N.W. 2. British. Research Assistant at the British Museum Laboratory. Trained in Analytical

Chemistry under the late Dr. Ludwig Mond, F.R.S., and the late Dr. B. Mohr, 1891–1896. Assistant at the Davy Faraday Research Laboratory of the Royal Institution, 1896–1918. Research Assistant at The British Museum Laboratory since 1920. (*Signed by*) Alexander Scott, H. J. Plenderleith, John W. Heath.

Prescott, James Arthur, The University, Adelaide, South Australia. British (England). Professor of Agricultural Chemistry at the Waite Agricultural Research Institute of the University of Adelaide. Papers on Soil Chemistry in the "Journal of Agricultural Science," VI, 111; VIII, 65, 111, 136; IX, 216; X, 177; XIII, 333; also Bulletins of the Sultanic Agricultural Society, Egypt. Research Scholar, Rothamsted Experimental Station, 1912–1916. Chief Chemist, Sultanic Agric. Soc., Egypt, 1916–1924. Proceedings, vol. 30, No. 123, 1914. (*Signed by*) Edward H. Rennie, E. J. Russell, H. B. Dixon, Arthur Lapworth, Robert Robinson, H. J. Page.

Robertson, John Monteath, Nether Fordun, Auchterarder, Perthshire. Scottish. Research Assistant. B.Sc. (Hons. Chem.), Glasgow, 1923. A.I.C., 1924. Strang-Steel Research Scholar, 1923–24. Carnegie Research Scholar, 1924–25. (*Signed by*) S. Horwood Tucker, T. S. Patterson, G. G. Henderson, R. Wright, David T. Gibson.

Rubenstein, Leon, Jesus College, Oxford (Rookwood, 87, Eaton Grove, Swansea). British. Research Student for Doctorate of Philosophy (Oxford University). First Class Honours, Degree of Bachelor of Science (Welsh Univ.). Bachelor of Science (Oxford Univ.). "Substitution in Vicinal Trisubstituted Benzene Derivatives" (November 1923). (*Signed by*) W. H. Perkin, S. G. P. Plant, J. F. S. Stone, R. H. Griffith, R. D. Haworth.

Singh, Malik Karam, Rawalpindi City. Indian (British subject). Paper Expert. I am a B.Sc. (Physics and Chemistry). Was granted a "State Technical Scholarship" by the Govt. of India for the study of the Paper-making industry in Gt. Britain and other Western countries. Before going to England I worked for about twenty months in the Bengal Paper Mills, Raneegunj (near Calcutta), during 1918–20. Joined College of Technology, Manchester, in 1920. During 1920–21 I completed in one year, a two years' course in paper making, and in the final examination I got a 1st class both in the theoretical and practical parts of the subject. I also studied the following subjects: Organic Chemistry, Physical Chemistry, Chemistry of Dyeing, Chemistry of the Colouring Matters, Economics, Chemical Engineering, Heat Engines, and Construction of Works. In 1921–22 (about 15 months) I received practical training in the following three paper mills, in Aberdeen, Scotland, making different classes of paper: (1) The Donside Paper Mills; (2) The Alex Pirie Paper Mills at Stoneywood, and (3) The Mugiemoss Paper Mills at Bucksburn. During 1922–24 I conducted a special research on about a score of Indian raw materials, with a view to ascertain their suitability for making paper. I have paid short visits lasting from one to ten days to about a score of other paper mills and paper mill machinery manufacture workshops. I have seen almost all the paper mills in India. (*Signed by*) John K. Wood, Frank Lee Pyman, F. M. Rowe.

Smith, Norman Heath, Hillcroft, Spencer Avenue, Leek, Staffs. British. Process Chemist, at present with Messrs. Anglo-Persian Oil Co., Ltd., Abadan, Persia. B.Sc. (Tech.). Post grad. research on vegetable oils; 2½ years with Messrs. The British Aluminium Co., Ltd., as Asst. Chemist, and over 2 years with Messrs. Anglo-Persian Oil Co., Ltd. (*Signed by*) Colin E. Spearing, S. W. Hayter, H. Harper.

Streather, Alec Thomas, 3, Wellington Road, Watford. British. Works Chemist. B.Sc. (Honours Chemistry), Birmingham, 1922. Associate Institute of Chemistry. (*Signed by*) G. T. Morgan, S. R. Carter, C. E. Wood, F. W. Pinkard.

Thurgood, John, "Roseleigh," Elmwood Ave., Harrow, Middx. British. Analytical and Research Chemist. Engaged for 4 years in laboratory of Dunlop Rubber Co., Birmingham. Graduated B.Sc. at Birmingham University in 1922. At present engaged as Assistant Chemist to British Oxygen Co., Ltd., N. Wembley. (*Signed by*) G. T. Morgan, C. E. Wood, E. Holmes.

Trew, Violet Corona Gwynne, 18, Adam Street, Portman Square, W. 1. British. Student at Bedford College (London University). Reading for an Honours Degree in Chemistry. (*Signed by*) J. F. Spencer, H. Crompton, P. V. McKie.

Uchida, Shojiro, 12, Shinryudo-Machi, Azabu-Ku, Tokio, Japan. Japanese. Research Chemist of the Fuel Research Board of Japan. Undergraduate of Department of Chemistry, College of Technology, University of Tokio, Japan. (*Signed by*) W. A. Batley, V. H. Legg, M. J. Burgess, F. V. Tideswell.

Walker, John Henry, A.R.T.C., A.I.C., Gourepore Works, Naihati, E.B. Ry., Bengal, India. Scotch. Chemist and Oil-mill Manager. Student Royal Technical College, Glasgow. Student with late Dr. J. Lewkowitsch. Sundry papers in *Analyst* and in *J.S.C.I.* Chemist and latterly mill-manager, Gourepore Co., Ltd., Linseed Oil. (*Signed by*) G. G. Henderson, Thomas Gray, F. J. Wilson.

Warren, Ernest Henry, 1, Chamber's Lane, Willesden Green, N.W. 10. English. Research Student. B.A., Cantab. (*Signed by*) Robert Robertson, Geo. Stubbs, P. J. Sageman.

Watt, James, Craiglockhart House, Slateford, Edinburgh. British. Writer to the Signet. Chairman of Directors, T. and H. Smith, Ltd., Chemical Manufacturers. F.R.S.E. (*Signed by*) James Walker, Alex. C. Cumming, Alexander Lauder.

Willis, William John, Hazel Mount, Carnforth, Lancs. English. Chief Valuer to Michael Faraday and Partners, 77, Chancery Lane, W.C. 2. 3 years' Assistant Demonstrator, Inorganic Chemistry, Barrow Technical School. 3 years' Lecturer on Metallurgy and Iron Foundry Practice, Bradford Technical College. 1st Class Honours Inorganic Chemistry, Science and Art Department. 1st Class Honours and Bronze Medal, City and Guilds of London, Iron and Steel Manufacture. 1st Class and Silver Medal, City and Guilds of London, Salt Manufacture. 8 years Analytical Chemist, Barrow Hematite Steel Co., Ltd. 6 years Chief Chemist and Assistant Works Manager, Yorkshire Iron and Coal Co., Ltd. 5 years Chief Valuer to Michael Faraday and Partners, Surveyors and Valuers. (*Signed by*) T. A. Henry, A. E. Bond, Harry W. Dixon.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2).

Beesley, William, Binnyston Gardens, Bangalore City, Mysore, India. British. Works' Chemist. Took course in Bleaching and Dyeing at the Manchester College of Technology. Technological Certificate and Silver Medallist in Dyeing, City and Guilds of London Institute. Six years Chemist Assistant with Messrs. Binny & Co., Ltd. Now Head Chemist, Bangalore Woollen Mills, India. (*Signed by*) E. Knecht.

Ecker, Howard, 1510 Dana Ave., Cincinnati, Ohio, U.S.A. American.

Research Director for The R. I. Johnston Paint Co., Cincinnati, Ohio. Graduate student from Ohio Mechanics Institute, Cin., Ohio. 1 year graduate work, Columbia College, N.Y. 6 years teaching at Ohio Mechanics Institute and for 3 years head of the department. Member of the American Chemical Society, Society of Chemical Industry, German Chemical Society. (*Signed by*) John H. Foulger.

Smith, Alexander, P.O. Box 103, Nairobi, Kenya Colony. Scot. Chemist and Managing Director, A. H. Wardle & Co., Ltd. Lecturer on chemistry for 2 years, School of Mines, South Africa. Pharmaceutical Society, minor certificate. Consulting Chemist to Kenya Marble Quarries. In charge Hygiene Laboratory (Dr. Kochs), Dar-es-Salaam, 12 months. (*Signed by*) G. T. R. Francis.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Association of British Chemical Manufacturers. British chemicals, their manufacturers and uses : being the official directory . . . containing a full list of members, with a classified list of British chemicals and a note of their industrial applications. London 1925. pp. 212. (*Reference.*) 10*s.* 6*d.* net.

From the Publishers : Messrs. Ernest Benn.

Indian Chemical Society. Quarterly Journal. Vol. I, etc. Calcutta 1924 +. (Two copies.) From the Society.

Institut International de Chimie Solvay. Premier conseil de chimie, tenu à Bruxelles du 21 au 27 Avril 1922. Rapports et discussions . . . sur cinq questions d'actualité. Paris 1925. pp. xvi + 336. ill. (*Reference.*) 30 *fr.* net.

From the Publishers : MM. Gauthier-Villars & Cie.

Namari, Ichitaro. The electrolytic separation of magnesium from magnesia. Sakai 1924. pp. iv + 160. ill. (*Recd.* 15/4/25.)

From the Author.

Philip, James Charles. Physical chemistry : its bearing on biology and medicine. 3rd edition. London 1925. pp. viii + 368. ill. 8*s.* 6*d.* net. (*Recd.* 7/5/25.) From the Author.

Rumbold, W. G. Bauxite and aluminium. (Imperial Institute Monograph on Mineral Resources.) London 1925. pp. x + 110. ill. 6*s.* net. (*Recd.* 17/4/25.) From the Director.

Scientific Worker, The, and the B.A.C. Bulletin. Official organ of the National Union of Scientific Workers and the British Association of Chemists. New series. Vol. I, etc. London 1924 +. (*Reference.*)

From the Publishers : The National Union of Scientific Workers.

Spring, Walthère. Œuvres complètes, publiées par la Société Chimique de Belgique. 2 vols. Bruxelles 1914–1923. pp. iv + 900, iv, 901 to 1860. ill. 40 *fr.* (*Recd.* 9/4/25.)

From the Société Chimique de Belgique.

Staudinger, Hermann. Introduction to qualitative organic analysis. Authorised translation by Walter Theodore Karl Braunholtz. London 1925. pp. xvi + 112. 6*s*. 6*d*. net. (*Recd.* 8/4/25.)
From the Publishers : Messrs. Gurney & Jackson.

Tables Annuelles de Constantes et données numériques de chimie, de physique et de technologie. Vol. V. 1917–1922. Part i. Paris 1925. pp. xlii + 804. (*Reference.*)
From the Comité International.

Thoms, Hermann. [Editor.] Handbuch der praktischen und wissenschaftlichen Pharmazie. Vol. III, Part ii. Vol. IV, Part i. Berlin 1925. pp. 289 to 544, 272. ill. *M*. 20. (*Recd.* 15/4/25.)
From the Publishers : Herren Urban & Schwarzenberg.

II. *By Purchase.*

Anderson, Robert J. The metallurgy of aluminium and aluminium alloys. New York 1925. pp. xxxii + 914. ill. 42*s*. net. (*Recd.* 27/4/25.)

Babbitt, Harold E. Sewerage and sewage treatment. 2nd edition. New York 1925. pp. xvi + 516. ill. 25*s*. net. (*Recd.* 13/5/25.)

Bragg, Sir William Henry, and Bragg, William Lawrence. *X*-rays and crystal structure. 5th edition. London 1925. pp. xii + 324. ill. 21*s*. net. (*Recd.* 13/5/25.)

Burrell, George A. The recovery of gasoline from natural gas, with a discussion of motor fuels. New York 1925. pp. 600. ill. 35*s*. net. (*Recd.* 13/5/25.)

Burton, Eli Franklin. The physical properties of colloidal solutions. 2nd edition. London 1921. pp. viii + 222. ill. 12*s*. 6*d*. net. (*Recd.* 21/4/25.)

Coffignier, Charles. Colours and varnishes. Translated from the French by A. Harvey. London 1925. pp. viii + 258. ill. 12*s*. 6*d*. net. (*Recd.* 13/5/25.)

Colloid Symposium Monograph. Papers presented at the second National Symposium on Colloid Chemistry, June 1924. Edited by Harry N. Holmes. New York 1925. pp. viii + 368. ill. 25*s*. net. (*Recd.* 21/4/25.)

Gough, Herbert John. The fatigue of metals. London 1924. pp. xx + 304. ill. 25*s*. net. (*Recd.* 13/5/25.)

Hatschek, Emil. [Editor.] The foundations of colloid chemistry; a selection of early papers bearing on the subject. Edited on behalf of the Colloids Committee of the British Association. London 1925. pp. 174. 18*s*. net. (*Recd.* 13/5/25.)

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, June 4th, 1925, at 8 p.m., Dr. Arthur W. Crossley, C.M.G., C.B.E., D.Sc., F.R.S., President, in the Chair.

The President referred to the loss sustained by the Society, through death, of Mr. Charles E. Soane, who was elected a Fellow on February 3rd, 1887, and who died on May 17th.

The President announced that the following address of congratulation had been sealed and will be presented on June 16th, 1925, to the Royal Institution on the occasion of the celebration of the Centenary of the discovery of benzene by Michael Faraday :

To the President, Officers and Members of the Royal Institution of Great Britain.

The Chemical Society welcomes the opportunity of associating itself with the Royal Institution in celebrating the centenary of the Discovery of Benzene by Michael Faraday, a discovery which was destined to have such far-reaching effects on the foundation and development of structural organic chemistry and to lead to the establishment of many new and important industries. We remember with pride that in 1868 the Chemical Society instituted a Triennial Lecture to commemorate the work of Faraday, for we recognise in him the pioneer of many of the principles underlying the chemical science of to-day.

We desire to join with the other Learned Societies and Academies of the world in offering our homage to the memory of this great and distinguished man.

Signed on behalf of the Chemical Society,

Arthur W. Crossley, *President.*
Jocelyn Thorpe, *Treasurer.*
T. Slater Price, } *Secretaries.*
C. S. Gibson, }
F. G. Donnan, *Foreign Secretary.*

Sealed in Council this Fourth Day of June, One Thousand Nine Hundred and Twenty Five.

Mr. W. A. Wightman was formally admitted a Fellow of the Chemical Society.

Certificates were read for the first time in favour of:

William Bouch O'Brien Goudielock, 28, Fairfield Lane, Barrow-in-Furness.
Jnanendra Nath Ray, M.Sc., The University, Manchester.
Phyllis Mary Sanderson, 7, Cresswell Place, S.W. 10.
Eric Alfred Speight, B.Sc., A.R.C.S., 61, Arthur Road, Wimbledon Park, S.W. 19.
Gordon Mitchell Wright, M.A., B.Sc., University Chemical Laboratory, Cambridge.

The following papers were read:

"The spatial structure of *cyclo*paraffins. Part I. A new aspect of Mohr's theory and the isomerism of decahydronaphthalene." By W. A. Wightman.

"Chenopodium oil. Part II. The hydrocarbon fraction." By T. A. Henry and H. Paget.

"Echitamine." By J. A. Goodson and T. A. Henry.

Ordinary Scientific Meeting, Thursday, June 18th, 1925, at 8 p.m., Dr. Arthur W. Crossley, C.M.G., C.B.E., D.Sc., F.R.S., President, in the Chair.

The President announced:

1. That, as Fellows would know, the Council has had before it for some time past the possibility of unifying chemical abstracts in pure and applied chemistry in the English language, and as stated in the Report of Council for 1923—1924, the Bureau of Chemical Abstracts was created to effect such unification. The Council, at its meeting that afternoon, had under consideration the following proposals of the Bureau, that

(1) The format adopted for the unified publications should be double column quarto.

(2) The type should be that now employed in the "A" Abstracts.

(3) The existing overlap, estimated to be at least 10%, should be eliminated,

as well as the further suggestion that, in the event of these proposals being adopted, one annual index covering both sections of the Abstracts should be supplied to all members of the two Societies concerned.

The Council has adopted the following resolution:

"That the Council concurs in the Bureau's proposals for the unification of the Abstracts in Pure and Applied Chemistry, and urges the Fellows, in the interests of co-operation and of

the consolidation of British Chemical Abstracts, to accept loyally such changes of format and arrangement as these proposals may involve."

It was further intimated that the proposals of the Bureau have also been accepted by the Council of the Society of Chemical Industry.

The President expressed the hope that Fellows would loyally support the efforts being made in the direction of unifying British chemical abstracts.

2. That the Faraday Society will hold a General Discussion on "Photochemical Reactions in Liquids and Gases" at Oxford on October 1st and 2nd next. The subject will be discussed under two main heads : (1) Einstein's Law of Photochemical Equivalence, (2) The Mechanism of Photochemical Reactions. Part I will be opened by Professor A. J. Allmand (King's College) and Part II by Professor M. Bodenstein (Berlin).

Fellows of the Chemical Society will be welcomed at this meeting, and it is hoped to accommodate all who attend the meeting at Exeter College and Lincoln College. Those desirous of attending are asked to communicate at once with the Secretary of the Faraday Society, 90, Great Russell Street, London, W.C. 1, from whom full particulars may be obtained.

3. That a communication has been received from the Committee of the van't Hoff Fund for the endowment of research in pure and applied chemistry. The amount from this fund available for distribution during 1926 is about 1400 Dutch florins.

A Committee, consisting of Professor A. F. Holleman (President), Professor F. M. Jaeger, Professor A. Smits, and Mr. J. P. Wibaut (Secretary), has been appointed to award Grants. Applications should be sent before November 1st, 1925, by registered post to : "Het Bestuur der Koninklyke Akademie van Wetenschappen, bestemd voor de Commissie van het 'van't Hofffonds,' Trippenhuis, Kloveniersburgwal, Amsterdam." Every applicant is requested to submit a detailed account of the manner in which he proposes to expend the grant and to state the reasons for which he makes his application.

Papers embodying the results of the research may be published in any journal, but acknowledgment must be made of the source of the grant. Copies of papers containing the results of the research must be forwarded to the Committee.

4. That Volume V of the Annual Tables of Constants and Numerical Data is now ready, and is obtainable from Monsieur Charles Marie (9, Rue de Bagneux, Paris VI) who will be glad to send particulars on application.

Messrs. J. B. Reed and P. W. B. Harrison were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of :

Joseph Raymond Dolphin, B.Sc., Chemical Department, The University, Birmingham.
Henry Wilfrid Keenan, 80, Upper Richmond Road, East Sheen, S.W. 14.
Bertram Grey Leatherbarrow, Hill Crest, Station Road, Brimington, Chesterfield.
Henry Nicholson, M.Sc., Aberlady, Osborne Road, Stockton-on-Tees.
Robert Saxon, B.Sc., Westfield Terrace, Baildon, Yorks.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2) :

Bertram Cuthbert, c/o The British Australian Cotton Association, Ltd. Oil Mills, Brisbane.
Albert Louis Auguste Sigot, Institut de Chimie, 2, Rue Goethe, Strasbourg.

Mr. H. C. Sayer and Dr. H. Burgess were elected Scrutators, and a ballot for the election of Fellows was held, the following subsequently being declared elected as Fellows :

Marion Alice Battie, B.Sc., A.I.C.
Maung Hla Baw.
William Beesley.
William Ambler Berry, B.Sc.
Joseph John Blackie.
Samuel Cyril Blacktin, M.Sc.
Neville Melton Bligh, A.R.C.S., A.I.C.
Hugh Alexander Millar Borland, M.Sc., A.R.C.S.
Nirmal Boran Brohmachary, B.Sc.
Gertrude Margaret Bullick, B.Sc.
Ralph Edgar Cable.
Thomas Anthony Canning.
Leslie Marshall Clark, B.A., Ph.D., A.I.C.
Clive Kear Colwell, B.A.
Jan Coops.
William George Corderoy, B.Sc.
Oswald Pilkington Cronshaw.
John Carroll Culbert.
John Alexander Currie, B.A., B.Sc.
Alexander John Dey.
Thomas Dillon, M.A., D.Sc.
Octave Charles Marie Dony.
Howard Ecker.
Stanley James Featherston.
Malcolm Sinclair Gaskill.
William Edward Gibbs, D.Sc.
Norman Hamer, Assoc.M.C.T.
Ernest Hartshorne, B.Sc.Tech.
Arthur Harvey.
Charles Richard Hennings, Ph.D.
James Hindle.
Noel Waterman Vere Jones.
Frank William Linch, M.Sc., F.I.C.
Charles Lipshaw.
Thomas Moore, B.Sc.
Ivor Gray Nixon.
Vincent Joseph Occleshaw, M.Sc., A.I.C.
Ernest Charles Padgham.
James Arthur Prescott, M.Sc., A.I.C.
John Monteath Robertson, B.Sc., A.I.C.
Leon Rubenstein, B.Sc.
Malik Karam Singh, B.Sc.
Alexander Smith.
Norman Heath Smith, B.Sc.Tech.
Alec Thomas Streather, B.Sc., A.I.C.
John Thurgood, B.Sc.
Violet Corona Gwynne Trew.
Shojiro Uchida.
John Henry Walker, A.R.T.C., A.I.C.
Ernest Henry Warren, B.A.
James Watt.
William John Willis.

The following papers were read :

" Investigations on the dependence of rotatory power on chemical constitution. Part XXVII. Some esters of *p*-toluene-sulphonic and sulphinic acids." By H. PHILLIPS.

" The enhanced reactivity of newly formed molecules. Part I. The conversion of cyclols into ketones." By F. R. Goss and C. K. INGOLD.

" Constituents of *Myoporum lætum*, Forst (' The Ngaio '). Part I." By F. H. McDOWALL.

" A synthesis of datiscetin." By J. KALFF and R. ROBINSON.

" The relative directive powers of groups of the forms RO– and RR'N– in aromatic substitutions. Part IV. A discussion of the observations recorded in Parts I, II, and III." By J. ALLAN, A. E. OXFORD, R. ROBINSON, and J. C. SMITH.

" A new aspect of the photochemical union of hydrogen and chlorine, and a quantitative study of the induction period." By R. G. W. NORRISH.

The Council has made the following Grants from the Research Fund :

	£	*s.*	*d.*
Bromination products of caronic acid. R. G. Atkinson. ...	12	0	0
Mechanism of tautomeric change. J. W. Baker	15	0	0
Photographic investigation of explosion waves. C. Campbell ...	5	0	0
Chemistry of the aminotriazole derivatives (*contd.*). P. K. Dutt.	5	0	0
Chemistry of the acridine molecule (*contd.*). P. K. Dutt ...	5	0	0
Ring-chain tautomerism. S. Dutt	10	0	0
Investigation and synthesis of ten-membered rings of the cryptopine type. G. A. Edwards	10	0	0
Contact electrification. F. Fairbrother	7	0	0
Oxidation of 5 : 6-benzo-1 : 1′-diethylcarbocyanine bromide. E. H. St. C. Flack	10	0	0
Oxidation of sesquiterpenes. D. T. Gibson	5	0	0
Action of thionyl chloride on hydroxybenzenes. A. Green ...	5	0	0
Structure of alkaloids and related compounds. J. M. Gulland...	10	0	0
Derivatives of methyl quinolines (*contd.*). D. Ll. Hammick ...	10	0	0
Some polarity effects in substituted stilbenes and tolanes. H. A. Harrison	10	0	0
Synthesis of alkaloids and allied compounds. R. D. Haworth ...	15	0	0
Investigation of the structure of Ciba Yellow (*contd.*). E. Hope	10	0	0
Experiments on the tetrahedral theory to S–N rings. R. F. Hunter	5	0	0
Action of aldehydes on aldehyde cyanohydrins in solution. B. H. Ingham	5	0	0
Reactivity of bivalent carbon. Mrs. E. H. Ingold	10	0	0
Correlation of additive reactions with tautomeric change (*contd.*). Mrs. E. H. Ingold	5	0	0
Mobility of the $\alpha\beta$-$\beta\gamma$ change in unsaturated acids and unsaturated ketones. J. D. Johnson	15	0	0

	£	s.	d.
Influence of *gem*-dimethyl grouping on the formation and ring closure of substituted adipic acids. J. Kracovski	12	0	0
The constitution of strychnine and of brucine. F. Lions ...	20	0	0
Acid chlorides of the type chlorothiol benzoyl chloride and their products. E. W. McClelland	5	0	0
Influence of various substituents on the reactivity of organic compounds. I. Cyanohydrin formation. R. H. F. Manske...	10	0	0
Further investigation of the "Rotary Stillhead." J. E. Myers	10	0	0
Investigation of heterocyclic compounds related to tetrahydrocarbazole. S. G. P. Plant	15	0	0
Stereochemistry of arsenic. R. Raper	10	0	0
Rapid thermal decomposition of certain organic compounds under reduced pressure. J. Reilly	7	10	0
Ring-chain tautomerism of the $\beta\beta$-disubstituted lævulic acids and their structures. E. Rothstein	20	0	0
(*a*) Substituted indole derivatives			
(*b*) Orientation in trisubstituted benzene derivatives (*contd.*). L. Rubenstein	5	0	0
Chemistry of the three-carbon system. L. F. Smith	12	0	0
Three-carbon tautomerism (*contd.*). E. A. Speight	15	0	0
The parachor and chemical constitution. S. Sugden	10	0	0
Influence of water vapour on reactions of the type: Solid $\rightleftarrows$ solid + gas. B. Topley	5	0	0
Physical properties of straight-chain alkyl benzenes and their derivatives (*contd.*). E. E. Turner	5	0	0
Investigation of sulphur trioxide (*contd.*). I. Vogel	5	0	0
Synthetical experiments in the *iso*quinoline series. R. Campbell	10	0	0
Separation of platinum from iridium and rhodium with special reference to complex nitrites. D. F. Withers	10	0	0
Total	£370	10	0

PUBLICATIONS FUND.

List of Donations and Subscriptions received from Fellows.

	Donations. £	s.	d.	*Subscriptions.* £	s.	d.	
Acworth, J. J.	50	0	0				
Albright, G. S.	10	0	0				
Andrews, L. W. ($20.00)	4	9	11				
Appleyard, P.				1	0	0	per annum
Atkinson, H. M.	10	0	0				
Audley, J. A.				10	0		,,
Backer, H. J.	1	0	0				
Bahadur, His Highness Maharaja Rana Sir Bhawani Singh	15	0	0				
Baker, H. B.				15	0	0	(£3 per annum for 5 years)
Barker, T. V.	2	0	0				
Barlow, H. W. L.	1	0	0				
Barnett, E. de B.	1	0	0				

	Donations.			*Subscriptions.*			
	£	*s.*	*d.*	£	*s.*	*d.*	
Barton, R.	2	0	0				
Bedford, C. S.				1	1	0	per annum
Beilby, Sir George	30	0	0				
Blackman, P.					3	0	,,
Boake, A.	5	0	0				
Boon, A. A.				1	0	0	,,
Borland, W. D.	10	10	0				
Borns, H.	10	0	0				
Boyle, M.					10	0	,,
Brady, O. L.				2	0	0	per annum for 5 years
Braunholtz, W. T. K.		10	0				
Brünnich, J. C.	10	0	0				
Bryant, J. J.	1	1	0				
Burgess, M. J.					10	0	per annum
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Carpmael, W.				1	1	0	,,
Carr, F. H.	5	5	0				
Carter, S. R.				1	0	0	,,
Caswell, A. E.					5	0	,,
Caven, R. M.				1	0	0	,,
Chapman, A. Chaston	10	10	0				
Chapman, D. L.	7	10	0				
Chattaway, F. D.	5	0	0				
Chikashigé, M.	5	0	0				
Clarke, H. T.	21	0	0				
Cohen, J. B.					10	0	,,
Colles, W. M.	1	1	0				
Collie, J. N.	10	0	0				
Colman, H. G.	10	0	0				
Cottrell, A.					10	0	,,
Cowburn, A. W.	5	0	0				
Cox, H. E.				1	1	0	per annum for 5 years
Crompton, H.	10	0	0				
Cross, C. F.	10	0	0				
Crossley, A. W.	20	0	0				
Crowle, R. S.				1	0	0	per annum for 5 years
Cuthbertson, L. M. G.	1	1	0				
Dakin, H. D.	10	0	0				
Denham, W. S.	10	0	0				
Dixon, H. B.	10	10	0				
Donnan, F. G.	5	0	0				
Doran, W.	1	0	0				
Douglas, J. R.					10	0	per annum
Dunn, F. P.				2	0	0	per annum for 5 years
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Dyer, B.	25	0	0				
Easterfield, T. H.	10	0	0				

	Donations.			*Subscriptions.*			
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Fryer, A. C.	2	2	0				
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Gilmour, R.	3	3	0				
Gonville, C. H. K.	2	2	0				
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Greenaway, A. J.	6	0	0				
Greeves, A.	5	0	0				
Hale, A. J.	2	0	0				
Hale, H. O.	1	0	0				
Hale, W. J.	10	0	0				
Harker, G.	2	0	0				
Hart, H. W.				1	0	0	per annum
Hartley, T.	5	5	0				
Hartung, E. J.				1	0	0	,,
Haworth, W. N.	5	0	0				
Heasman, B. R.	2	0	0				
Heilbron, I. M.	10	0	0				
Hellon, R.				1	1	0	(deceased)
Henderson, G. G.	5	0	0				
Henley, The Hon. F. R.	5	0	0				
Henry, T. A.	10	0	0				
Henstock, H.	1	1	0				
Heycock, C. T.	10	10	0				
Hill, C. A.	10	0	0				
Hills, H. F.	5	0	0				
Hills, W.	5	5	0				
Hinkel, L. E.	1	0	0				
Hislop, R. F.				5	0		per annum
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Hooper, E. Grant	5	0	0				
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	Donations.			*Subscriptions.*			
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Jenkins, J. H. B.	5	5	0				
Kenner, J.		5	0				
Kipping, F. S.	10	0	0				
Kynaston, J. W.	.	.	.	1	0	0	,,
Lamb, E.	5	0	0				
Lampitt, L. H.	1	10	0				
Lapworth, A.	20	0	0				
Lattey, W. T.	2	0	0				
Laurie, A. P.	.	.	.	1	0	0	,,
Law, H. E.	10	0	0				
Leathes, J. B.	15	0	0				
Lessner, C.	10	0	0				
Levy, S. I.	.	.	.	1	1	0	,,
Lewis, E. W.	.	.	.		10	0	,,
Lewis, W. C. McC.	.	.	.	1	0	0	,,
Lewis, W. J.	5	0	0				
Liveing, G. D.	50	0	0				
Liversidge, A.	25	0	0				
Low, A. M.		10	0				
Lowry, T. M.	5	0	0				
Lyons, A. B.	.	.	.	1	0	0	,,
Macalpine, F. C.	.	.	.	1	0	0	per annum from 1926
McBain, J. W.	1	0	0				
McEwen, B. C.	3	3	0				
McGowan, G.	1	1	0				
McKenzie, A.	3	3	0				
Main, H.	1	1	0				
Marcan, A.	5	5	0				
Martin, George, H.	1	0	0				
Martindale, W. H.	.	.	.	1	0	0	per annum
Martineau, S.	25	0	0				
Matthews, D. J.	.	.	.		10	6	,,
Maxwell, M.	10	0	0				
Meldrum, A. N.	7	10	0				
Mellor, J. W.	7	10	0				
Menzies, R. C.	4	4	0				
Merrett, W. H.	.	.	.	1	1	0	for 1924
Miers, Sir Henry A.	8	0	0				
Moody, G. T.	.	.	.	5	0	0	per annum for 10 years
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	Donations. £ *s.* *d.*	*Subscriptions.* £ *s.* *d.*
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Silberrad, C. A.	. . .	1 0 0 per annum.
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Walker, A.	50 0 0	
Walker, Sir James	10 0 0	
Warwick, G. R.	1 0 0	
Whiteley, M. A.	. . .	10 0 ,,
Williams, W. Carleton	10 0 0	
Wilson, C. P.	. . .	10 0 ,,
Wilson, F. J.	5 0 0	
Withers, J. C.	. . .	1 0 0 ,,
Woolcock, W. J. U.	5 0 0	
Wright, W. T.	10 0 0	
Wynne, W. P.	. . .	5 5 0 per annum for 4 years
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Young, J. H.	2 0 0	
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The Library will be closed for Stocktaking from Monday, August 3rd, until Saturday, August 15th, 1925 (inclusive). During the

following four weeks (August 17th to September 12th), the Library will close daily at 5 p.m.

LIST OF FELLOWS, 1925.

The List of Fellows for 1925 is now in active preparation and will be supplied to those Fellows who make application to the Assistant Secretary by the 31st July, 1925. In order that the new List may be as complete as possible, Fellows are invited to notify any change of address, or other alteration, before that date.

BERICHTE, 1915–1924.

Sets of the Berichte from 1915 to 1924 (10 years) are now offered to Fellows of the Society at £22, carriage extra. Application should be made to Mr. S. E. Carr.

List of papers, or Abstracts thereof, received between May 22nd and June 18th, 1925. (This List does not include the titles of papers which have been read at a Scientific Meeting or which have appeared in the Journal.)

"A low voltage standard cell." By H. Mastin.

"Hydrogen and oxygen electrode titrations of some dibasic acids and of dextrose." By H. T. S. Britton.

"Sulphur sesquioxide." By I. Vogel and J. R. Partington.

"The relation of homogeneous to catalysed reactions. The catalytic decomposition of hydrogen iodide on the surface of gold." By C. N. Hinshelwood and C. R. Prichard.

"The decomposition of carbon monoxide in the corona due to alternating electric fields. Part I." By M. Crespi and R. W. Lunt.

"The formation and stability of spiro-compounds. Part XII. Further evidence for the multiplanar configuration of the *cyclo*heptane ring." By J. W. Baker.

"The condensed ternary system phenol–water–salicylic acid." By C. R. Bailey.

"The hydration of strong electrolytes and some properties of salt solutions." By J. N. Sugden.

"The action of sulphur on amines. Part III. *o*-, *m*-, and *p*-Chloroanilines." By H. H. Hodgson and J. H. Wilson.

"The system sodium sulphite–sodium hydroxide–water." By D. L. Hammick and J. A. Currie.

"Synthetical experiments in the *iso*quinoline group. Part V. Synthesis of substances allied to oxyberberine." By R. D. Haworth, W. H. Perkin, and H. S. Pink.

"Amino benzothiazoles. Part II. The naphthylamino naphthiazoles and their bromo derivatives." By R. F. Hunter.

"Negative adsorption : the surface tensions and activities of some aqueous salt solutions." By A. K. Goard.

"The structure of α-campholytic acid. A correction." By J. P. C. Chandrasena, C. K. Ingold, and J. F. Thorpe.

"The interaction of carbon dioxide and hydrogen on the surface of tungsten." By C. N. Hinshelwood and C. R. Prichard.

"Note on potassium antimonoxalate." By L. H. A. Holmes and E. E. Turner.

"Studies on the Walden inversion. Part IX. The influence of the solvent on the sign of the product in the conversion of β-bromo-β-phenylpropionic acids to β-hydroxy-β-phenylpropionamides." By G. Senter and A. M. Ward.

"'Co-ordination' and the periodic table." By I. Aucken.

"Anode phenomena in the electrolysis of potassium ethyl malonate." By J. B. Robertson.

"The isomerism of the styryl alkyl ketones. Part II. The isomerism of the homologues of 2-hydroxystyryl, and of 3-methoxy-, and 4-hydroxy-styryl methyl ketones." By A. McGookin and D. J. Sinclair.

"Hydrogen electrode studies of the precipitation of hydroxides. Part I. Magnesium, manganous, ferrous, cobalt, nickel, and thorium." By H. T. S. Britton.

"Stereoisomeric azo-dyes." By G. T. Morgan and D. G. Skinner.

"4- and 4′-Methoxybenzoylbenzoin." By H. Greene.

"The relative rates of conversion of phenoxyphenyldichloroarsine and its chloro-derivatives into chlorophenoxarsines." By E. Roberts and E. E. Turner.

"Chemistry of petroleum. Part II. The action of sodium hypochlorite on types of sulphur compounds found in petroleum distillates." By S. F. Birch and W. S. G. P. Norris.

"Derivatives of δ-*o*-aminobenzoylvaleric acid." By M. J. Paterson and S. G. P. Plant.

"The action of formic acid on certain sesquiterpenes." By J. M. Robertson, C. A. Kerr, and G. G. Henderson.

"Syntheses of disulphoxides." By D. T. Gibson, C. J. Miller, and S. Smiles.

"The effect of gum arabic and other emulsifiers on the acid hydrolysis of esters in heterogeneous systems." By R. C. Smith.

"Lithium arc spectrum for polarimetric use." By P. C. Austin.

"Bismuth dihydride." By E. J. Weeks and J. G. F. Druce.
"Reduction product of the hydroxyanthraquinones. Part VI." By A. G. Perkin and G. Yoda.
"A wandering of the acetyl group during methylation." By O. Kubota and A. G. Perkin.
"The supposed formation of 1 : 2 : 4-oxadi-imine rings from nitroso-compounds and methylenearylamines." By G. N. Burkhardt, A. Lapworth, and E. B. Robinson.
"The reaction of bromine with aliphatic acids. Catalytic effect of acyl halides." By H. B. Watson.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Clarke, Frank Wigglesworth. The data of geochemistry. 5th edition. Washington 1924. pp. 842. (*Recd.* 26/5/25.)
From the Author.

Daniels, George William. Refrigeration in the chemical industry. London 1925. pp. x + 141. ill. (*Recd.* 29/5/25.)
From the Publisher : Mr. A. J. Rayment.

Eastman Kodak Company. Abridged scientific publications from the Research Laboratories. Vol. VIII, 1924. Rochester, N.Y. 1925. pp. 156 + vi. ill. (*Reference.*)
From the Eastman Kodak Company.

Imperial College Chemical Society. Journal. Vol. IV, containing the papers read during the session 1924—1925. London 1925. pp. 54. ill. (*Reference.*) From the Society.

Klar, M. The technology of wood distillation with special reference to the methods of obtaining the intermediate and finished products from the primary distillate. Translated [from the 2nd German edition] by Alexander Rule. With an additional chapter by the translator. London 1925. pp. xvi + 496. ill. 25*s.* net. (*Recd.* 8/6/25.)
From the Publishers : Messrs. Chapman & Hall.

Morrice, Alexander. A treatise on brewing : wherein is exhibited the whole process of the art and mystery of brewing the various sorts of malt liquor; with practical examples upon each species. Together with the manner of using the thermometer and saccharometer; elucidated by examples, and rendered easy to any capacity, in brewing London porter [etc.]. London 1802. pp. [xii] + v to 180 + [xii]. ill. (*Reference.*)
From Dr. Alexander Scott.

National Benzole Association and University of Leeds. *Joint Benzole Research Committee.* Second report. London 1925. pp. 246. ill. (*Recd.* 18/5/25.)

From the National Benzole Association.

Organic Syntheses: an annual publication of satisfactory methods for the preparation of organic chemicals. Vol. IV. Edited by Oliver Kamm [and others]. New York 1925. pp. viii + 90. 7*s.* 6*d.* net. (*Recd.* 22/5/25.)

From the London Publishers: Messrs. Chapman & Hall.

Tiba. Revue Générale de Teinture Impression Blanchiment Apprêt et de Chimie Textile et Tinctoriale et Revue de la Soie Artificielle. Year II, etc. Paris 1924 +. (*Reference.*)

From the Publishers.

II. *By Purchase.*

Birtwhistle, George. The principles of thermodynamics. Cambridge 1925. pp. x + 164. ill. 7*s.* 6*d.* net. (*Recd.* 10/6/25.)

Chemical Engineering and Chemical Catalogue 1925: a catalogue of heavy and fine chemicals, raw material, machinery, plant and equipment applicable to production industries. Compiled with the co-operation of leading British manufacturers by Leonard Hill. Edited by Dudley Maurice Newitt. London 1925. pp. 260. ill. (*Reference.*) 21*s.* net.

Dukes, Cuthbert. The bacteriology of food. London 1925. pp. xii + 180. ill. 7*s.* 6*d.* net. (*Recd.* 10/6/25.)

Friend, John Newton. [Editor.] A text-book of inorganic chemistry. Vol. III. Part i. The alkaline earth metals. By May Sybil Burr (née Leslie). London 1925. pp. xxvi + 346. (*Reference.*) 20*s.* net.

Howe, H. E. [Editor.] Chemistry in industry: a coöperative work intended to give examples of the contributions made to industry by chemistry. New York 1924. pp. xiv + 372. ill. 6*s.* net. (*Recd.* 16/4/25.)

Jörgensen, Alfred. Micro-organisms and fermentation. 5th edition. Revised by the Author with the assistance of S. H. Davies. London 1925. pp. xiv + 468. ill. 30*s.* net. (*Recd.* 10/6/25.)

Johnson, J. B. Materials of construction. Rewritten by M. O. Withey and James Aston. Edited by F. E. Turneaure. 6th edition. New York 1925. pp. xx + 866. ill. 30*s.* net. (*Recd.* 13/5/25.)

Klooster, Henry S. van. Lecture and laboratory experiments in physical chemistry. 2nd edition. Easton, Pa. 1925. pp. x + 274. ill. 12*s.* net. (*Recd.* 15/5/25.)

Ladoo, Raymond B. Non-metallic minerals: occurrence—preparation—utilization. New York 1925. pp. viii + 686. ill. 30*s*. net. (*Recd.* 10/6/25.)

Lord, Leonard J. Practical butter and cheese making. London 1925. pp. 200. ill. 10*s*. 6*d*. net. (*Recd.* 13/5/25.)

Mellor, Joseph William. Modern inorganic chemistry. New edition. London 1925. pp. xx + 1104. ill. 12*s*. 6*d*. net. (*Recd.* 15/5/25.)

Newman, Frank Herbert. The production and measurement of low pressures. London 1925. pp. 192. ill. 16*s*. net. (*Recd.* 10/6/25.)

North, Sydney H., and Garbe, J. B. Low temperature distillation, home oil supply and the utilization of "waste" coal. London 1925. pp. vi + 216. ill. 15*s*. net. (*Recd.* 13/5/25.)

O'Brien, W. B. Factory practice in manufacture of azo dyes. Easton, Pa. 1924. pp. viii + 176. ill. 22*s*. 6*d*. net. (*Recd.* 16/4/25.)

Parry, Ernest John. Parry's cyclopædia of perfumery. 2 vols. London 1925. pp. vi + 840. (*Reference.*) 36*s*. net.

Richmond, Henry Droop. The laboratory book of dairy analysis. 3rd edition. London 1925. pp. viii + 118. ill. 5*s*. net. (*Recd.* 15/5/25.)

Sim, James. Steam condensing plant in theory and practice. London 1925. pp. xiv + 272. ill. 18*s*. 6*d*. net. (*Recd.* 10/6/25.)

Thompson, Maurice de Kay. Theoretical and applied electrochemistry. Revised edition. New York 1925. pp. xx + 552. ill. 20*s*. net. (*Recd.* 13/5/25.)

Thomson, Sir Joseph John. The electron in chemistry: being five lectures delivered at the Franklin Institute, Philadelphia. [Philadelphia] 1923. pp. vi + 144. ill. 10*s*. 6*d*. net. (*Recd.* 15/5/25.)

Vedder, Edward B. The medical aspects of chemical warfare. With a chapter on the naval medical aspects of chemical warfare by Duncan C. Walton. Baltimore 1925. pp. xvi + 328. ill. 32*s*. 6*d*. net. (*Recd.* 26/5/25.)

Wells, Harry Gideon. The chemical aspects of immunity. New York 1925. pp. 254. 20*s*. net. (*Recd.* 18/5/25.)

Williams, George Bransby. Sewage disposal in India and the East. Calcutta 1924. pp. x + 230. ill. 17*s*. 6*d*. net. (*Recd.* 13/5/25.)

Wood, Thomas Barlow. Animal nutrition. London 1924. pp. viii + 226. 4*s*. 6*d*. net. (*Recd.* 15/5/25.)

World Power Conference, First. London 1924. Transactions. 5 vols. London [1925]. pp. xxiv + 1506, xviii + 1600, xvi + 1502, xx + 1816. (*Reference.*)

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, October 15th, 1925, at 8 p.m., Dr. ARTHUR W. CROSSLEY, C.M.G., C.B.E., D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows :

	Elected.	*Died.*
Richard Burtles	May 3rd, 1923.	July 3rd.
Charles Frederick Chandler	Feb. 1st, 1872.	Aug. 25th.
William Henry Deering	April 1st, 1869.	Sept. 5th.
William Joseph Dibdin	April 15th, 1880.	June 8th.
Samuel Jackson	Dec. 15th, 1892.	July 27th.
Francis Robert Japp	Feb. 6th, 1879.	Aug. 1st.
Reginald A. Joyner	Dec. 6th, 1917.	Oct. 8th.
Daniel Rankin Steuart	Dec. 15th, 1881.	Aug. 1st.
Leonard E. Vlies	Feb. 21st, 1918.	July 26th.

The PRESIDENT announced that :

1. The first of the two Informal Lectures to be held this Session will be delivered in the Rooms of the Society on Thursday, November 26th, 1925, by Professor R. Robinson, D.Sc., F.R.S., who has chosen as his subject :

> " Recent Researches on the Structural Relationships of Some Plant Products."

Special attention is drawn to the fact that the lecture will be delivered at 6 *o'clock* instead of at 8 *o'clock* as stated on the meeting card.

2. Following the innovation made in October, 1923, it has been decided to hold next month a united dinner for British Chemists. The dinner, to be called " British Chemistry Dinner " is under the auspices of the Chemical Society, the Institute of Chemistry, the Society of Chemical Industry, the Association of British Chemical Manufacturers, the Institution of Petroleum Technologists, the Society of Public Analysts, the Bio-Chemical Society, the Oil and Colour Chemists' Association, and the Chemical Industry Club,

and will be held at the Connaught Rooms, Great Queen Street, W.C. 2, on Friday, November 13th, 1925, at 6.30 for 7 p.m. Dr. W. R. Ormandy, Chairman of the Chemical Industry Club, will preside.

The price of the tickets is 15*s.* each (not including wine) for lady or gentleman, and as the accommodation is limited to about 400, early application is advisable.

Besides the Loyal Toasts, there will be only two other Toasts, namely, " The Profession and Industry of Chemistry " and " The Guests." After dinner, there will be dancing and musical items.

Application for tickets (15*s.* each), with remittance, should be sent to the Secretary of the Chemical Industry Club, 2, Whitehall Court, S.W. 1.

3. The Selection Committee of the Harrison Memorial Prize will meet shortly to consider the award of the Harrison Prize.

The Prize, of the value of about £150, is to be awarded to the chemist of either sex being a natural born British subject and not at the time over thirty years of age, who, in the opinion of the Selection Committee, during the previous five years has conducted the most meritorious and promising original investigations in any branch of pure or applied chemistry and published the results of those investigations in a scientific periodical or periodicals.

Provided that in the opinion of the Selection Committee there is a candidate of sufficient distinction to warrant an award of the Prize, the award is to be made in December, 1925.

The Selection Committee is prepared to receive applications, nominations or information as to candidates eligible for the Prize. Any such information must be received by The President, The Chemical Society, Burlington House, Piccadilly, W. 1, not later than Tuesday, December 1st, 1925.

4. As Fellows are already aware, the Council has approved the proposals of the Bureau of Chemical Abstracts (see Procs. for June, 1925), aiming at the unification of abstracts of chemical papers in this Country. As a consequence of the arrangements made, " British Chemical Abstracts " will appear as from January, 1926, in two sections, namely, A (Pure Chemistry) and B (Applied Chemistry), and will be in the same format and type, without overlap, and with one common index at the end of the year. The format adopted is that at present employed for the " B " Abstracts; beginning, therefore, with January, 1926, Fellows will receive the Abstracts in Pure Chemistry in quarto double-column size. This clearly means a break with the past, so far as the Chemical Society is concerned, but the Council trusts that in the interests of co-operation the Fellows will accept these changes with loyalty.

5. The price of the Annual Reports for 1925, Vol. XXII, will be the same as for Vol. XXI, namely 5*s*. 6*d*. post free to those Fellows who apply by Christmas Day, 1925. Application should be made to the Assistant Secretary, and must be accompanied by a remittance for 5*s*. 6*d*.

6. Volume I of the Memorial Lectures has been reproduced by a photographic process, and is now on sale at the Publishers, Messrs. Gurney & Jackson, 33, Paternoster Row, E.C. 4, price to Fellows 9*s*. post free.

7. Sets of the Berichte from 1915–1924 (10 years) can be obtained on application to the Assistant Secretary at the reduced price of £22, plus carriage.

8. In continuance of the arrangement made with the American Chemical Society, the *Journal of the American Chemical Society*, *Industrial and Engineering Chemistry*, and *Chemical Abstracts*, can be obtained by Fellows at the following reduced rates :

Price for any one journal $7.25, post free,
Price for any three journals $17.50, post free,

while *Chemical Reviews* is offered to Fellows at $4.50, post free. Applications should be made as soon as possible to Dr. Charles L. Parsons, Secretary, American Chemical Society, 1709, G. Street N.W., Washington, D.C., U.S.A.

The *Journal of Physical Chemistry* is obtainable by Fellows at $8.00 post free, published at $10.00. Application should be made to the *Journal of Physical Chemistry*, Ithaca, N.Y., U.S.A.

9. A meeting of the Research Fund Committee will be held in December next. Applications for Grants, to be made on forms obtainable from the Assistant Secretary, must be received on or before Tuesday, December 1st, 1925. Applications from Fellows will receive prior consideration.

All persons who received Grants in December, 1924, or in December of any previous year, whose accounts have not been closed by the Council, are reminded that Reports must be returned by December 1st.

The following were formally admitted Fellows of the Chemical Society : G. M. Bullick, C. G. Trew, I. C. P. Smith, W. G. Corderoy, E. H. Warren, I. A. Smith, C. F. Flint, R. R. Garran, N. M. Bligh, and E. C. Padgham.

Certificates were read for the first time in favour of :

Robert Leslie Andrew, Dominion Laboratory, Wellington, New Zealand.
Louis Baissac, Curepipe Road, Mauritius.
William Francis Barker, Ph.D., Rhodes University College, Grahamstown, S. Africa.
Ralph Basden, The Technical College, Newcastle, N.S.W.

Frank Bell, 11, Edwy Parade, Gloucester.
Arthur Neville Copnall Bennett, B.Sc., 27, Dale Road, Luton.
John Cecil Bird, B.Sc., A.I.C., 72, Dyne Road, Kilburn, N.W. 6.
Lionel Christopher William Birkett, B.Sc., Moor House, North Road, Spennymoor.
James Boyd, F.I.C., P.O. Box 1162, Johannesburg.
Frank Symonds Bradhurst, c/o Messrs. Holbrooks, Ltd., Danks Street, Waterloo, Sydney.
John Hildred George Carlile, B.Sc., A.R.C.S., 29, Orlando Road, Clapham, S.W. 4.
Leslie James Chalk, B.Sc., 14, Shrubbery Road, Southall.
Rama Charan, B.Sc., B.Sc.Tech., 12, Bank Road, Allahabad.
Edward Mortimer Crowther, D.Sc., F.I.C., Rothamsted Experimental Station, Harpenden, Herts.
Frank Edwin Dickinson, Research Establishment, Sutton Oak, St. Helens.
William Donovan, M.Sc., Dominion Laboratory, Wellington, New Zealand.
John Stanley Dunn, M.A., Ph.D., A.I.C., 39, Victoria Park, Cambridge.
Edwin Francis Edwards, c/o Messrs. Holbrooks, Ltd., Waterloo, Sydney.
John Moelwyn Edwards, 92, Jamaica Road, Rotherhithe, S.E. 16.
James Walter Shanks Gemmell, B.Sc., Helen's Villa, Fleming Place, St. Andrews.
Francis Reginald Glover, 98/100, St. Peters Street, Nottingham.
Felix John Theodore Grigg, M.Sc., A.I.C., Government Buildings, Christchurch, New Zealand.
John Hall, M.Sc., A.I.C., 202, Burton Road, Derby.
Herbert Sim Hirst, B.Sc., Trinity College, Cambridge.
Toru Iwadare, c/o Banyu Pharmaceutical Co., Ltd., 174, Shimomeguro, Tokyo, Japan.
David Christopher Mendis Jayewardene, Fern Bank, Moratuwa, Ceylon.
Charles Benjamin Johnson, 134, Preston New Road, Blackburn.
Walter Idris Jones, Ph.D., B.Sc., 7, Manor Street, Cambridge.
Charles King, 141, Bath Street, Glasgow.
Frederick Karl Victor Koch, B.Sc., A.R.C.S., 9, Crossfield Road, Hampstead, N.W. 3.
Charles Dudley Langford, B.Sc., A.R.C.S., 43, Ashbourne Avenue, Temple Fortune, N.W. 11.
Henry Guinness de Laszlo, B.A., Ph.D., 3, Fitzjohn's Avenue, Hampstead, N.W. 3.
Sam Lenher, B.A., 15, Gordon Street, W.C. 1.
William Macartney, c/o Messrs. Grattan & Co., Ltd., Belfast.
William Francis Martin, F.I.C., 27, Shandon Crescent, Edinburgh.
Arthur Moore, Highfield, Oakworth, Keighley.
John Blackburn Murgatroyd, 90, St. George's Square, S.W. 1.
Chitsukhlal Hiralal Nanavati, 80, Esplanade Road, Fort, Bombay.
Anna Maria O'Mara, 83, Elsham Road, Holland Park, W. 14.
Norman Frederick Parker, B.A., A.I.C., 45, Sellons Avenue, Harlesden, N.W. 10.
Marjorie Ellen Pring, B.Sc., 66, St. Augustine's Avenue, S. Croydon.
Herbert Charles Roberts, 15, Estcourt Terrace, Headingley, Leeds.
George Baty Scott, 37, Woodbridge Road, Knowle, Bristol.
Rupert Boswood Scammell, B.Sc., c/o Messrs. F. H. Faulding & Co., Ltd., Castlereagh Street, Redfern, Sydney.
Upo Shin, Agricultural Farm, Mandalay.

Dalip Singh, Ph.D., near Tehsil P.O., Lahore.
William Veale Thorpe, B.A., 270, Balham High Road, S.W. 12.
William Milburn Towler, B.Sc., 28, Denton Avenue, Roundhay, Leeds.
David Traill, B.Sc., 58, Chalmers Street, Dunfermline.
Donald Morrison Turner, 40–42, Lexington Street, W. 1.
Geoffrey Turner, B.Sc., 85, Winchester Avenue, Leicester.
Frederick Henry Webb, St. Malo, Jameson Road, Harpenden, Herts.
Hugh Amphlett Williams, 249, Kennington Road, S.E. 11.
Robert Harding Williams, 131, Anlaby Road, Hull.
John James Benjamin Wolfe, 24, Greyhound Road, Hammersmith, W. 6.
John Frederick Zimmermann, 17, Stile Hall Gardens, Chiswick, W. 4.

The following papers were read :

"The effect of ultra-violet light on dried hydrogen and oxygen." By H. B. Baker and M. Carlton.

"A new per-oxide of barium." By M. Carlton.

"The production of oxide-films on copper at ordinary temperatures." By U. R. Evans.

"The structural isomerism of the oximes. Part III. The benzil-monoximes." By A. H. Atack and F. W. Atack.

List of papers, or abstracts thereof, received between June 18th and October 15th, 1925. (This list does not include the titles of papers which have been read at an Ordinary Scientific Meeting, or which have appeared in the Journal.)

"The action of sulphuretted hydrogen on a neutral solution of potassium permanganate." By H. B. Dunnicliff and S. Dayal.

"Note on the preparation of thiocarbanilide." By S. J. C. Snedker.

"Studies with the microbalance. Part II. The photochemical decomposition of silver chloride." By E. J. Hartung.

"Preparation, hydrolysis and reduction of the isomeric fluorobenzyl bromides." By J. B. Shoesmith and R. H. Slater.

"The action of silica on electrolytes. Part II." By A. F. Joseph and H. B. Oakley.

"The formation and growth of silver nuclei in the decomposition of silver oxalate." By J. Y. Macdonald and C. N. Hinshelwood.

"Researches in the menthone series. Part I." By J. Read and A. M. R. Cook.

"Studies in adsorption by the application of optical methods. Fixation by dispersoids of methylene-blue within the disperse phase." By A. Fodor and R. Riwlin.

"The physical chemistry of the metal–ammonium complexes. Part I. The blue of the copper–ammonium complexes." By S. S. Bhatnagar, M. Prasad and D. Nath.

"The correlation of absorption spectra with ionisation in violuric acid." By R. A. Morton and A. H. Tipping.

"Absorption spectra and lactam-lactim tautomerism." By R. A. Morton and E. Rogers.

"The heat of combustion of salicylic acid." By E. Berner.

" An electrometric and phase rule study of some basic salts of copper." By H. T. S. Britton.

" The distribution of pyridine between water and benzene." By R. M. Woodman and A. S. Corbet.

" The velocity of decomposition of oxalic acid in solution." By D. L. Watson.

" The absorption of gases in colloidal solutions." By A. Gatterer.

" A circulation apparatus for gases." By N. G. Chatterji and G. I. Finch.

" 2 : 4-Dinitrophenylhydrazine as a reagent for aldehydes and ketones." By O. L. Brady and G. V. Elsmie.

" The methylation of the oximes of benzil." By O. L. Brady and H. M. Perry.

" The alkaline oxidation of some carbohydrates by means of dyestuffs, considered quantitatively." By E. Knecht and E. Hibbert.

" Unstable states of solutions of sodium behenate." By M. E. Laing and collaborators.

" Note on the preparation of *p*-nitrophenylhydrazine." By H. H. Hodgson and H. G. Beard.

" The preparation of 2-nitro-1-halogen naphthalenes and of β-nitronaphthalene." By H. H. Hodgson and E. Kilner.

" The swelling and dispersion of some colloidal substances in ether–alcohol mixtures." By E. W. J. Mardles.

" The relationship of salts in dilute aqueous solution as determined by their influence on the critical solution temperature of the system phenol–water." By J. H. Carrington, L. R. Hickson, and W. H. Patterson.

" The colorimetric dissociation constants of dinitrocatechol and dinitroresorcinol." By F. C. Laxton, E. B. R. Prideaux, and W. H. Radford.

" The cyanine dyes. Part IX. The mechanism of the condensations of quinaldine alkiodides in presence of bases." By W. H. Mills and R. Raper.

" Dibenzylquinaldine." By W. H. Mills and A. T. Akers.

" The action of nitrous acid upon amides and other ' amino ' compounds." By R. H. A. Plimmer.

" Olefinic terpene ketones from the volatile oil of flowering *Tagetes glandulifera*. Part I." By T. G. H. Jones and F. B. Smith.

" On the interaction between copper and sulphuric acid." By C. W. Rogers.

" Trypanocidal action and chemical constitution. Part II. Arylamides of 4-aminophenyl-arsinic acid." By H. King and W. O. Murch.

" The butyl esters of the simpler amino-acids. Part I." By W. T. J. Morgan.

" The influence of salts in ethyl alcohol solution on the mutual miscibility temperature of the system ethyl alcohol–paraffin." By E. J. Howard and W. H. Patterson.

" Condensations of the sodium derivatives of trimethylene glycol and glycerol." By A. Fairbourne and G. E. Foster.

" An investigation of the effect of differential aëration on corrosion by means of electrode potential measurements." By A. L. McAulay and F. P. Bowden.

" The recognition of allotropy in metals." By D. Stockdale.

" Solubility influences. Part I. The effect of some salts, sugars, and temperature on the solubility of ethyl acetate in water." By S. Glasstone and A. Pound.

" Experiments on the synthesis of apofenchocamphoric acid. Preparation of αα-dimethyl-β′-carboxyadipic acid." By K. C. Roberts.

"Electrometric study of the reactions between alkalis and silver nitrate solutions." By H. T. S. Britton.

"Electrometric separation of the iodide, bromide and chloride of silver." By H. T. S. Britton.

"Reduction products of the hydroxyanthraquinones. Part VII." By W. B. Miller and A. G. Perkin.

"Chloro-derivatives of *m*-hydroxybenzaldehyde." By H. H. Hodgson and H. G. Beard.

"The nitration of *m*-bromophenol." By H. H. Hodgson and F. H. Moore.

"The reduction of arsenic compounds by sodium hyposulphite. The production of subsulphides of arsenic." By W. Farmer and J. B. Firth.

"The electrical conductivities of hydrochloric acid and potassium chloride in water and acetone–water mixtures." By T. K. Brownson and F. M. Cray.

"Metallocyclic compounds. Part I. Compounds of tellurium." By H. D. K. Drew.

"The action of hydrogen fluoride on compounds of selenium and tellurium. Part I. Selenium dioxide." By E. B. R. Prideaux and J. O'N. Millott.

"The resolution of an asymmetric arsenic compound into its optically active forms." By W. H. Mills and R. Raper.

"The electrical conductivity of phosphorus pentachloride." By G. W. F. Holroyd, H. Chadwick, and J. Mitchell.

"Hydrogen electrode studies of the precipitation of basic chromates, borates and carbonates." By H. T. S. Britton.

"The relation between chemical constitution and pungency in acid amides." By E. C. S. Jones and F. L. Pyman.

"The rate of reaction of bromine with aqueous formic acid." By D. L. Hammick, W. K. Hutchison and F. R. Snell.

"The quaternary salts of benzoxazoles." By L. M. Clark.

"$\gamma\gamma'$-Dichloropropyl sulphide." By G. M. Bennett and A. L. Hock.

"Synthesis in the thianthren series. Part II." By M. Sen and J. N. Rây.

"Some lactonic esters derived from phenacyl bromide by condensation with ethyl sodiomalonate and analogous substances." By R. M. Rây and J. N. Rây.

"The velocity of decomposition of heterocyclic diazonium salts. Part I. Diazonium salts of the pyrazole and pyrazolone series." By J. Reilly and D. Madden.

"Orientating effects in the diphenyl series." By H. G. Dennett and E. E. Turner.

"The relative directive influence of polar and steric effects on ring closure." By R. W. J. Smith and E. E. Turner.

"The configuration of the ammonium ion." By W. H. Mills and E. H. Warren.

"Symmetrical substitution derivatives of trimethylene bromide and pentamethylene bromide." By W. H. Mills and L. Bains.

"Further studies on a new chlorinating agent preparation of polychloro-derivatives of toluene." By O. Silberrad.

"The equilibrium in the systems aluminium sulphate–copper sulphate–water and aluminium sulphate–ferrous sulphate–water at 25°." By V. J. Occleshaw.

"Reactions of the meso-hydroxyanthrones." By M. A. Matthews.

"The influence of different nuclei on the absorption spectra of substances." By J. E. Purvis.

"The occurrence of sylvestrene." By B. S. Rao and J. L. Simonsen.

"The partial formaldehyde vapour pressures of aqueous solutions of formaldehyde. Part II." By W. Ledbury and E. W. Blair.

"Trypanocidal action and chemical constitution. Part III. Arsinic acids containing the glyoxaline nucleus." By I. E. Balaban and H. King.

"The preparation of tertiary arsines by the Friedel-Crafts reaction." By A. F. Hunt and E. E. Turner.

"Equilibrium in the system : $CH_3COOCH_3+H_2O \rightleftharpoons CH_3OH+CH_3COOH$." By G. J. Burrows.

"The parachor and chemical constitution. Part III. Orientation isomerism in aromatic compounds." By S. Sugden and H. Wilkins.

"The aluminioxalates of some optically active bases." By T. B. Child, E. Roberts, and E. E. Turner.

"On the equilibrium between methylformate, methanol and hydrogen, and some related equilibria." By J. A. Christiansen.

"Hydrogen electrode studies of the reactions between solutions of salts of weak metallic bases and the acetate, oxalate and tartrate of sodium, with a note on the effect of dextrose on zirconium chloride solution." By H. T. S. Britton.

"The conversion of *r*-phenyl-α-naphthyl-glycollic acid into ketones." By A. McKenzie and H. J. Tattersall.

"Studies of equilibrium in systems of the type $Al_2(SO_4)_3$–$M''SO_4$–H_2O. Part II. Aluminium sulphate–nickel sulphate–water at 30°." By R. M. Caven and T. C. Mitchell.

"The system silver sulphate–aluminium sulphate–water at 30°." By R. M. Caven and T. C. Mitchell.

"Change of crystal habit of some salts when crystallised from silicic acid gel." By H. A. Fells and J. B. Firth.

"The ionic activity product of water in glycerol–water mixtures." By J. Colvin.

"2-*m*-Xylidino-5-ethoxy-4 : 5-dihydrothiazole." By V. K. Nimkar and F. L. Pyman.

"The change in the absorption spectra of aromatic nitro-compounds in liquid ammonia with time." By W. E. Garner and H. F. Gillbe.

"Nitrosyl sulphuric acid. Part I." By G. A. Elliott, L. L. Kleist, and H. W. Webb.

"The action of acetylenetetrabromide on organic bases." By J. D. Fulton.

"Production of *cyclo*telluripentanedionedichlorides." By G. T. Morgan (with F. J. Corby, O. C. Elvins, E. Jones, R. E. Kellett, and C. J. A. Taylor).

"Interactions of tellurium tetrachloride and monoketones." By G. T. Morgan and O. C. Elvins.

"A note on the sulphonation of 4-chloro-phenol." By J. M. Gauntlett and S. Smiles.

"Some analogues of adrenalone. Part I." By F. Matthews.

"The relationship between the optical rotatory powers and the relative configurations of optically active compounds. Part II. The relative configurations of the optically active mandelic acids and β-phenyl-lactic acids." By G. W. Clough.

Synthesis of 2 : 3 : 5-trimethyl glucose." By J. C. Irvine and J. W. H. Oldham.

"The oxidation of certain sesquiterpenes with chromyl chloride and chromic acid." By D. T. Gibson, J. M. Robertson, and J. Sword.
"Tesla-luminescence spectra. Part VI. Some amino-derivatives." By W. H. McVicker, J. K. Marsh, and A. W. Stewart.
"Glyceryl glucoside." By H. S. Gilchrist and C. B. Purves.
"A comparison of methods of measuring the polarity of surfaces." By N. K. Adam, R. S. Morrell, and R. G. W. Norrish.
"cyclo*Hexane*spirocyclo*hexane*." By W. S. G. P. Norris.
"The effect of heat on chloral hydrate." By J. D. Mounfield and J. K. Wood.
"The solubilities of sodium, potassium and calcium ferrocyanides. Part I." By M. P. Applebey and M. Farrow.
"Isomeric change of aromatic compounds. Part I. The conversion of diacylanilides into acylaminoketones." By A. W. Chapman.
"Nitrosyl sulphuric acid." By F. J. Wilson and H. W. Webb.
"The constitution of the metallic ozonides." By E. C. C. Baly and R. W. Riding.
"The influence of substituents on the stability of Schiff's bases. Part I. Hydrolysis of nitro- and methoxy-benzylidene anilines." By E. M. Langman, W. Healey, and P. K. Dutt.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Abderhalden, Emil. [Editor.] Handbuch der biologischen Arbeitsmethoden. Abt. I, Chemische Methoden, Teil 6, Heft. iii, Abt. III, Physikalisch-chemische Methoden, Teil A, Heft v. Berlin 1925. pp. [268] + xxiv, [136]. ill. *M.* 12.30, *M.* 5.70. (*Recd.* 12/9/25.) From the Publishers: Herren Urban & Schwarzenberg.

Australian Journal of Experimental Biology and Medical Science. Vol. I, etc. Adelaide 1924 +. (*Reference.*)
From the Publishers.

Berry, Arthur John. Volumetric analysis: with a chapter on simple gravimetric determinations. 3rd edition. Cambridge 1925. pp. viii + 152. ill. 9*s.* net. (*Recd.* 9/10/25.)
From the Syndics of the Cambridge University Press.

Brun, P. L'industrie des cyanures. Paris 1925. pp. 470. ill. 20 *fr.* net. (*Recd.* 22/9/25.)
From the Publisher: M. Gaston Doin.

Bunbury, Hugh Mills, and Davidson, Alfred. The industrial applications of coal tar products. London 1925. pp. xii + 284. 42*s.* net. (*Recd.* 7/9/25.)
From the Publishers: Messrs. Ernest Benn.

Cohen, Julius Berend, and Ruston, Arthur G. Smoke: a study of town air. [2nd] edition. London 1925. pp. xii + 108. ill. 8*s.* 6*d.* net. (*Recd.* 14/10/25.)
From the Publishers: Messrs. Edward Arnold & Co.

Eastman Kodak Company. Aerial haze and its effect on photography from the air. Rochester, N.Y. 1923. pp. 84. ill. (*Recd.* 16/6/25.) From the Eastman Kodak Company.

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From the Publishers : Messrs. Crosby Lockwood & Son.

Hausbrand, Eugen. Principles and practice of industrial distillation. Translated from the 4th German edition by Edward Howard Tripp. London 1925. pp. xx + 300. ill. 21*s.* net. (*Recd.* 12/9/25.) From the Publishers : Messrs. Chapman & Hall.

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Jacobson, Carl Alfred. A pronouncing chemical formula speller and contest guide. Baltimore 1925. pp. xviii + 280. (*Reference.*) 20*s.* net.

From the English Agents : Messrs. Baillière, Tindall & Cox.

Leathes, John Beresford, and Raper, Henry Stanley. The fats. 2nd edition. London 1925. pp. viii + 242. 12*s.* 6*d.* net. (*Recd.* 15/10/25.)

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Martindale, William Harrison, and Westcott, William Wynn. The extra pharmacopœia. 18th edition. Vol. II. London 1925. pp. xlii + 728. (*Reference.*) 20*s.* net.

From the Publishers : Messrs. H. K. Lewis & Co.

Matagrin, A. L'industrie des produits chimiques et ses travailleurs. Paris 1925. pp. xviii + 486. ill. 12 *fr.* net. (*Recd.* 7/9/25.) From the Publisher : M. Gaston Doin.

Medical Research Council. Special Report Series, No. 71. The aetiology and pathology of rickets from an experimental point of view. By V. Korenchevsky. London 1922. pp. 172 + 18 plates. 4*s.* net.

—— Special Report Series, No. 77. Studies of rickets in Vienna

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—— Special Report Series, No. 93. Experimental rickets : the effect of cereals and their interaction with other factors of diet and environment in producing rickets. By Edward Mellanby. London 1925. pp. 66 + 40 plates. 3*s*. 6*d*. net.

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Meijer, Willem. Pyrazolonen. Groningen 1925. pp. 84. (*Recd*. 16/6/25.) From the Publisher : M. Edzo Venema.

Menschutkin, Boris N. A short course of chemistry for technical colleges and universities. Leningrad 1925. pp. 128. [In Russian.] (*Recd*. 12/8/25.) From the Author.

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Plimmer, Robert Henry Aders, and Plimmer, Violet G. Food and health. London 1925. pp. vi + 64. ill. 3*s*. 6*d*. net. (*Recd*. 15/10/25.) From the Publishers : Messrs. Longmans, Green & Co.

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Thoms, Hermann. [Editor.] Handbuch der praktischen und wissenschaftlichen Pharmazie. Vol. II, part iii; Vol. III, part iii. Berlin 1925. pp. [384] + viii, [288]. ill. *M.* 14, *M.* 10. (*Recd.* 11/8/25.) From the Publishers : Herren Urban & Schwarzenberg.

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II. *By Purchase.*

Allen, Herbert Stanley. Photo-electricity. 2nd edition. London 1925. pp. xii + 320. ill. 18*s.* net. (*Recd.* 9/10/25.)

Alterthum, Hans. Wolfram : Fortschritte in der Herstellung und Anwendung in den letzten Jahren. Braunschweig 1925. pp. viii + 112. *M.* 4.30. (*Recd.* 19/6/25.)

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Becquerel, Jean. La radioactivité et les transformations des éléments. Paris 1924. pp. 208. ill. 5 *fr.* (*Recd.* 22/6/25.)

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Christiansen, Walter G. Organic derivatives of antimony. New York 1925. pp. 230. 15*s*. net. (*Recd.* 9/10/25.)

Clément, Louis, and Rivière, C. Matières plastiques; soies artificielles. Paris 1924. pp. 528. ill. 55 *fr*. net. (*Recd.* 22/7/25.)

Councell, R. W. Apologia alchymiæ: a re-statement of alchemy. London 1925. pp. xii + 88. 5*s*. net. (*Recd.* 16/6/25.)

Curie, Madame Pierre. L'isotopie et les éléments isotopes. Paris 1924. pp. 210. ill. 22.50 *fr*. (*Recd.* 22/6/25.)

Dixon, Walter Ernest. A manual of pharmacology. 6th edition. London 1925. pp. xii + 478. ill. 18*s*. net. (*Recd.* 9/10/25.)

Dodds, Edward Charles, and Dickens, Frank. The chemical and physiological properties of the internal secretions. London 1925. pp. xiv + 214. ill. 8*s*. 6*d*. net. (*Recd.* 9/10/25.)

Dubovitz, Hugo. Chemische Betriebskontrolle in der Fettindustrie. Berlin 1925. pp. vi + 136. ill. *M*. 6.90. (*Recd.* 26/6/25.)

Elliot, Cyril. Distillation in practice. London 1925. pp. 188. ill. 6*s*. net. (*Recd.* 14/10/25.)

Feuerfest. Zeitschrift für Gewinnung, Bearbeitung, Prüfung und Verwendung feuerfester Stoffe. Year I, etc. Leipzig 1925 +. (*Reference.*)

Gillett, Horace Wadsworth, and Mack, E. L. Molybdenum, cerium and related alloy steels. New York 1925. pp. 300. ill. 20*s*. net. (*Recd.* 12/6/25.)

Goodwin, Harold. Autoclaves and high pressure work. London 1925. pp. 166. ill. 6*s*. net. (*Recd.* 14/10/25.)

Gurwitsch, Leo. Wissenschaftliche Grundlagen der Erdölverarbeitung. 2nd edition. Berlin 1924. pp. vi + 400. ill. *M*. 18 net. (*Recd.* 22/7/25.)

Hamilton, Alice. Industrial poisons in the United States. New York 1925. pp. xii + 590. 21*s*. net. (*Recd.* 9/10/25.)

History of the Great War. Medical Services. Vol. II. Including . . . gas warfare, and gas poisoning in tanks and mines. Edited by Sir William Grant Macpherson [and others]. London 1923. pp. viii + 622. ill. 25*s*. net. (*Recd.* 20/6/25.)

Houben, Josef. Die Methoden der organischen Chemie. 3rd edition. Vol. I. Allgemeiner Teil. Leipzig 1925. pp. xxviii + 1340. ill. (*Reference.*) *M*. 75.

Kershaw, G. Bertram. Sewage purification and disposal. 2nd

edition. Cambridge 1925. pp. xii + 364. ill. 18*s*. net. (*Recd.* 9/10/25.)

Kershaw, John Baker Cannington. Fuel economy and smoke prevention: being the 3rd edition of "Smoke prevention and fuel economy" by W. H. Booth and J. B. C. Kershaw. London 1925. pp. xiv + 268. ill. 16*s*. net. (*Recd.* 9/10/25.)

Langton, Harold McKee. Blacks and pitches. London 1925. pp. 179. ill. 15*s*. net. (*Recd.* 14/10/25).

Le Blanc, Max. Lehrbuch der Elektrochemie. 11th and 12th edition. Leipzig 1925. pp. viii + 391. ill. *M*. 13. (*Recd.* 22/6/25.)

Lewis, William Cudmore McCullagh. A system of physical chemistry. 4th edition. Vol. II. Thermodynamics. London 1925. pp. viii + 490. ill. 15*s*. net. (*Recd.* 26/6/25.)

McKee, Ralph H. [and others]. Shale oil. New York 1925. pp. 326. ill. 22*s*. 6*d*. net. (*Recd.* 9/10/25.)

Nametkin, S. Die Umlagerung alizyklischer Kerne ineinander. (Sammlung, Vol. XXVIII.) Stuttgart 1925.

Patten, Nathan van. Bibliography of the corrosion of metals and its prevention. Kingston, Canada 1924. pp. iv + 186. (*Reference.*) 20*s*. net.

Poggendorff, Johann Christian. Biographisch-literarisches Handwörterbuch. Vol. V. 1904 to 1922. Edited by P. Weinmeister. Part i. Leipzig 1925. pp. iv + 696. (*Reference.*) *M*. 60.

Pringsheim, Hans, with the collaboration of Jesaia Leibowitz. Zuckerchemie. Leipzig 1925. pp. xii + 322. *M*. 18. (*Recd.* 19/6/25.)

Smith, Sydney. Forensic medicine: a text-book for students and practitioners. London 1925. pp. xiv + 498. ill. (*Reference.*) 21*s*. net.

Tammann, Gustav. A text-book of metallography: chemistry and physics of the metals and their alloys. Translated from the 3rd German edition . . . by Reginald Scott Dean and Leslie Gerald Swenson. New York 1925. pp. ii + 388. ill. 26*s*. net. (*Recd.* 16/6/25.)

[United States] National Research Council. *Division of Engineering and Industrial Research.* Marine structures, their deterioration and preservation: report of the Committee on Marine Piling Investigations. By William G. Atwood and A. A. Johnson [and others]. Washington, D.C. 1924. pp. viii + 534. ill. 31*s*. 6*d*. net. (*Recd.* 12/6/25.)

World List of Scientific Periodicals published in the years 1900–1921. London 1925. pp. xii + 499. (Two copies.)

III. *Pamphlets.*

(a) *From Professor P. Phillips Bedson.*

Austin, Leonard. Demonstration of rescue-apparatus, Felling, August 31st, 1907. (From the *Trans. Inst. Mining Engineers*, 1908.) ill.

Fernandes, Francis Vito. The Indian school of Chemistry. The researches of Professor Ray and his pupils at Presidency College. (From the *Presidency College Magazine*, 1915, **1**.)

French Commission on the Use of Explosives in the Presence of Fire-damp in Mines. Report. Translated by W. J. Bird and M. Walton Brown. 3 parts. Newcastle-upon-Tyne 1890–91. pp. 164. ill.

Morewood, A. Palmer. Shaw's gas tester, for detecting the presence of small percentages of gas in colliery workings. London 1896. pp. 18. ill.

North of England Institute of Mining and Mechanical Engineers. Report of the Committee appointed to enquire into the explosion of an air receiver at Ryhope Colliery. (From the *Trans. N. England Inst. Min. & Mech. Eng.*, 1888, **37**.) ill.

Smythe, John Armstrong. Two newly-discovered whin-dykes on the coast of Northumberland. (From the *Trans. Nat. Hist. Soc. Northumberland*, 1914, N.S. **4**).

—— On nitrosopinene. London 1898. pp. 19.

Trobridge, Frederick George. Über die Ester- und Amid-Sauren der Itaconsäure. Beuel a. Rh. 1910. pp. 36.

(b) *Miscellaneous.*

Anderson, L. A. P., Howard, Albert, and Simonsen, John Lionel. Studies on lathyrism. I. (From the *Indian J. Med. Research*, 1925, **12**.)

Gortner, Ross Aiken, and Hoffman, Walter Fred. Quantitative estimation of chlorides and sulphates in expressed plant tissue fluids. (From the *Bot. Gaz.*, 1924, **77**.)

Hendrick, James. Some characters of Scottish soils. (From the *Trans. Highland & Agric. Soc. of Scotland*, 1925.)

Mason, Frederick Alfred. An introduction to the literature of chemistry for senior students and research chemists. Oxford 1925. pp. 42.

Miller, Lewis B. Adsorption by aluminium hydrate considered as a solid solution phenomenon. (From the *U.S. Public Health Reports*, 1924, **39**.)

Mines Department. *Safety in Mines Research Board.* Second Annual report, 1923, etc. London 1924 +.

—— Paper No. 7. Explosives in Mines Research Committee. Second report 1924, etc. London 1925 +.

—— Paper No. 8. The ignition of fire-damp. By Hubert Frank Coward and Richard Vernon Wheeler. London 1925. pp. 25. ill.

—— Paper No. 9. The lag on ignition of firedamp. By C. A. Naylor and Richard Vernon Wheeler. London 1925. pp. 16. ill.

—— Paper No. 10. Firedamp explosions within closed vessels. The effects of turbulence. By G. B. Maxwell and Richard Vernon Wheeler. London 1925. pp. 12. ill.

Ministry of Health. Final Report of the Departmental Committee on the use of preservatives and colouring matters in food. London 1924. pp. 84.

Monier-Williams, Gordon Wickham. The solubility of glazes and enamels used in cooking utensils. (*Ministry of Health Reports on Public Health and Medical Subjects.* No. 29.) London 1925. pp. iv + 17.

National Association of Master Bakers, Confectioners and Caterers. Reports on research at the National Bakery School (Borough Polytechnic Institute), London, conducted by Charles Dorée and John Kirkland. (From the *Nat. Assoc. Review*, 1925.)

National Physical Laboratory. *Metrology Department.* Verification of weights: testing of balances: determination of densities. 1925. pp. 28.

Perkin, Frederick Mollwo. Recent progress in the peat problem. Paper read before the British Association at Southampton on August 27th, 1925. London 1925. pp. 24. ill.

Puig, P. Ignacio. Teoria de las valencias positivas y negativas. Barcelona 1924. pp. 31. ill.

Puiggari, Hugo. Fenómenos de transporte eléctrico en un hidrosol de oxido férrico. Trabajo presentado al 1er Congreso Sudamericano de Quimica. Buenos Aires 1924. pp. 11.

Radium. Le vingt-cinquième anniversaire de la découverte du radium (1898–1923). [Paris n.d.] pp. 86.

Rau, Madyar Gopal. The constituents of some Indian essential oils. Part XVI. (From the *Indian Forest Records*, 1924, **11**.)

Rau, Madyar Gopal and Simonsen, John Lionel. The constituents of some Indian essential oils. Part XVII. (From the *Indian Forest Records*, 1925, **11**.)

DEC 22 19

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, November 5th, 1925, at 8 p.m., Dr. ARTHUR W. CROSSLEY, C.M.G., C.B.E., D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows :

	Elected.	Died.
John Young Buchanan	June 21st, 1877.	Oct. 16th.
Harold James Cross	Feb. 15th, 1917.	Oct. 17th.
Francis Jones	Dec. 4th, 1873.	Oct. 22nd.
Charles Etty Potter	Dec. 5th, 1912.	Sept. 13th.

The PRESIDENT announced that Professors C. S. Gibson, G. T. Morgan, J. F. Thorpe, and W. P. Wynne, have been appointed by the Council to represent the Society on the Bureau of Chemical Abstracts, and that Professors T. M. Lowry, J. W. McBain, and J. C. Phillip will represent the Society on the Editorial Board of the Journal of Physical Chemistry, together with Professor F. G Donnan, appointed by the Faraday Society.

Certificates were read for the first time in favour of :

Harold Frederic Betts, B.Sc., 17, The Broadway, Broadstairs.
Edward Britnell, B.Sc., 9, Osterley Avenue, Isleworth.
Reginald John Bromfield, 141, Constantine Road, N.W. 3.
Francis Hereward Burstall, B.Sc., 12, Adelaide Road, Teddington.
Archer John William Butterfield, 163, Northumberland Park, N. 17.
John William Corran, B.Sc., Ph.D., A.I.C., Research Laboratory, Carrow Works, Norwich.
John Harold Cottier, 52, Aspen Grove, Lodge Lane, Liverpool.
John Horsfall Dyde, 18, Dean Road, Scarborough.
George Malcolm Dyson, B.A., B.Sc., Ph.D., 36, Hillsborough Road, E. Dulwich, S.E. 22.
Alfred Eccles, B.Sc., 18, Cambrian Terrace, Holbeck, Leeds.
George Albert Elliott, M.Sc., 263, Kennington Road, S.E. 11.
Eric Bertram Evans, B.Sc., 2, Boxmoor Terrace, Southchurch, Southend.
Elinor Katharine Ewbank, B.A., 22, Park Crescent, Oxford.

Elizabeth Monica Openshaw Farrow, M.A., 37, Chalfont Road, Oxford.
Oliver Free, B.A., The Lodge, Mansfield College, Oxford.
William Marshall Freeman, 1, Temple Gardens, Temple, E.C. 4.
Eva Florence Gee, The Station, L.N.E.R., Howsham, Lincoln.
George Vincent Hall, B.Sc., 6, Borough Road, Bridlington.
William Rowan Hare, 220, Eastfield, Peterborough.
Walter Healey, 28, Gooder Lane, Brighouse.
Thomas Henderson, M.C., M.A., B.Sc., Guildford Grammar School, West Australia.
Syed Husain, M.Sc., 112, Gower Street, W.C. 1.
Gilbert Jessop, M.Sc., Ph.D., 453, Glossop Road, Sheffield.
Brian Charles Lavers Kemp, B.A., Wellington College, Berks.
Banarsi Das Laroia, B.A., B.Sc., 3, Oxford Road, Teddington.
John Joseph Lennon, M.Sc., 6, Bartlemas Road, Oxford.
Ivan Roy McHaffie, B.A., M.Sc., 37, King Henry's Road, N.W. 3.
Neil McLean, M.A., B.Sc., 127, Blenheim Place, Aberdeen.
Leslie George Manchester, B.Sc., 557, Green Lanes, Hornsey, N. 8.
William Alfred Nottage Markwell, 26, Huntsmoor Road, S.W. 18.
Charles Henry Lawrence Miller, 50, Rowden Road, Beckenham.
Horace Winston Palmer, B.Sc., 15, Hollingdean Terrace, Brighton.
Austin McDowell Patterson, Antioch College, Yellow Springs, Ohio, U.S.A.
Ernest Phillis, B.Sc., 22, Fairford Terrace, Dewsbury Road, Leeds.
Jonathan Pollitt, B.A., 17, Caversham Avenue, Palmers Green, N. 13.
Charles Raymond Porter, M.Sc., A.I.C., 126, Linden Road, Bournville, Birmingham.
Evan Emrys Price, B.Sc., Rock House, Heathfield, Swansea.
Rose Rachel Sass, B.Sc., Newnham College, Cambridge.
Albert Sciver, B.Sc., A.I.C., 84, Vineyard Hill, Wimbledon Park, S.W. 19.
Frederick Francis Percival Smith, B.A., B.Sc., Peterhouse, Cambridge.
Robert Frederick Smith, 254, Higham Hill Road, Walthamstow, E. 17.
William Ernest Soper, B.Sc., 50, Aislibie Road, Lee, S.E. 12.
Herbert Kenneth Southern, B.Sc., Government Laboratory, Strand, W.C. 2.
Frank Harland Swire, 152, Queen's Road, Halifax.
Harold James Tattersall, B.Sc., Ph.D., 141, Thorold Road, Ilford.
Elvera Annie Tricker, 319, Norwich Road, Ipswich.
Norman Leopold Tyler, 9, St. Paul's Gardens, Spennymoor.
Herbert Ward Vernon, B.Sc. 245, Albert Road, N. 22.
Ewart Harrod Williams, B.Sc., A.I.C., 31, Thornsbeach Road, Catford, S.E. 6.
Gwyn Williams, B.Sc., Cae Ffynnon, Llandudno Junction.
John Laurence Wiltshire, B.Sc., 36, Fordel Road, Catford, S.E. 6.
Wilfred Fisher Wyatt, M.Sc., North Anston, Nr. Sheffield.

The following were formally admitted Fellows of the Chemical Society: W. J. V. Ward, H. F. Halliwell, R. J. W. Le Fèvre, I. J. Faulkner, J. Thurgood, and T. W. Jones.

The following papers were read:

"Further studies on a new chlorinating agent. Preparation of polychloro-derivatives of toluene." By O. Silberrad.

"The configuration of the ammonium ion." By W. H. Mills and E. H. Warren.

The following paper was taken as read :

" Ring-chain tautomerism. Part XV. The phenol-succineins and -glutareins." By S. Dutt.

Ordinary Scientific Meeting, Thursday, November 19th, 1925 at 8 p.m., Professor W. P. Wynne, D.Sc., F.R.S., Vice-President in the Chair.

The Chairman referred to the loss sustained by the Society, through death, of the following Fellows :

	Elected.	Died.
John Lloyd T. Jones	Feb. 7th, 1901.	Nov. 12th.
Frank George Pope	Feb. 18th, 1909.	Oct. 29th.
Robert Llewellyn Taylor	Jan. 15th, 1874.	Nov. 8th.

The Chairman announced that :

1. The Council has decided that the next Annual General Meeting and Dinner to take place on Thursday, March 25th, 1926, shall be held in Manchester. A local Sub-Committee has been appointed to make arrangements and full particulars will be announced later.

2. An Informal Meeting will be held in the Rooms of the Society on Thursday, December 17th, immediately after the conclusion of the formal business of the Ordinary Scientific Meeting at 8 p.m. Light refreshments will be provided, and smoking will be permitted, except on the Library Floor. The Council will welcome assistance from Fellows who can add to the interest of the Meeting by showing experiments or exhibiting apparatus, and those able to do so are requested to communicate with the Assistant Secretary not later than Monday, December 7th.

The following were formally admitted Fellows of the Chemical Society : Cyril C. Harris, John S. Carter, and T. H. Clare.

Certificates were read for the first time in favour of :

William Blakey, jun., B.A., 14, Marshall Road, Cambridge.
Herbert Clayton, M.A., B.Sc., The Dyson Perrins Laboratory, South Parks Road, Oxford.
John Charles Forsyth, 62, Worcester Street, Christchurch, New Zealand.
Ankarath Sankunni Mannadi Nayar, M.B., B.S., Ph.D., The Medical College, Madras.
William Bennett Price, B.Sc., The Laurels, Woolwich Road, Belvedere.
Madhavlal Sukhlal Shah, M.Sc., 22, Oxford Road, Putney, S.W. 15.
George Ernest Thompson, 7, Campbell Road, Bow, E. 3.
Bernard William Town, B.Sc., A.R.C.S., 79, The Grove, Hammersmith, W. 6.
Victor Martin Trikojus, B.Sc., Queen's College, Oxford.
Henry Woolf, P.O. Box 14, Broken Hill, Northern Rhodesia.

The following Certificate has been authorised by the Council for presentation to ballot under Bye-Law I (2) :

Edgar Calvin Le Roy Miller, M.D., Medical College of Virginia, Richmond Va., U.S.A.

The following papers were read :

" The constitution of the metallic ozonides." By E. C. C. Baly and R. W. Riding.

" Studies of dynamic isomerism. Part XX. Amphoteric solvents as catalysts for the mutarotation of the sugars." By T. M. Lowry and I. J. Faulkner.

" Studies of valency. Part V. Absorption spectra of halogen and sulphonic derivatives of camphor. Origin of the ketonic absorption band." By T. M. Lowry and G. Owen.

" Studies of valency. Part VI. General and selective absorption of halogen derivatives of methane. The origin of general absorption." By T. M. Lowry and R. R. Sass.

The following paper was taken as read :

" Studies of valency. Part VII. Surface polarity and the reaction of ethylene and chlorine. The effect of the adsorbed water layer." By R. G. W. Norrish and G. G. Jones.

List of papers, or abstracts thereof, received between October 16th and November 19th, 1925. (This list does not include the titles of papers which have been read at an Ordinary Scientific Meeting, or which have appeared in the Journal.)

" Polymerisation of β-glucosan. The constitution of synthetic dextrins." By J. C. Irvine and J. W. H. Oldham.

" The action of mercurous nitrate on chloroauric acid." By W. B. Pollard.

" The freezing of inorganic hydrogels." By J. R. I. Hepburn.

" The bromination of some 5-substituted 1-phenylbenzthiazoles." By R. F. Hunter.

" Studies on the dependence of optical rotatory power on chemical constitution. Part VI. Rotatory powers of phenyl, *o*-, *m*-, *p*-tolyl and β-naphthyl derivatives of *d*-camphorimide and *d*-camphoramic acid." By B. K. Singh and A. N. Puri.

" Transformations of the sugar nitrates." By J. W. H. Oldham.

" Studies in colour and constitution. Part I. The positional bathochromic influence of the methylthiol group, alone, and in conjunction with the methoxy-group." By H. H. Hodgson and F. W. Handley.

"The photochemical oxidation of hydriodic acid in ultra-violet light. Part I." By T. Moore.

"Ring-chain tautomerism. Part XVII. Instances showing how glutaric derivatives can simulate succinic compounds." By S. Dutt.

"A theory of colour on the basis of molecular strain. The effect of chromophoric superposition." By S. Dutt.

"The influence of the intensity of illumination on the velocity of photochemical changes." By F. Briers, D. L. Chapman, and E. Walters.

"The salting-out effect. The influence of electrolytes on the solubility of iodine in water." J. S. Carter.

"Germanium. Part II. Germanium tetrachloride and its ammonia compounds." By W. Pugh and J. S. Thomas.

"The action of alcoholic soda and potash upon chloronitrobenzene." By D. H. Richardson.

"The partial pressures of aqueous ethyl alcohol." By H. J. E. Dobson.

"A comparison of some of the physical properties of the alkali cyanates and azides." By J. A. Cranston and A. Y. Livingstone.

"Reactions for nitrites." By B. C. McEwen.

"Lead dihydride and lead tetrahydride." By E. J. Weeks.

"Some reactions of organic thiosulphates." By H. B. Footner and S. Smiles.

"Air oxidation of titanous and vanadous sulphates." By A. S. Russell.

"Complex formation in lead nitrate solutions. Part II. The quaternary system potassium nitrate–lead nitrate–barium nitrate–water." By S. Glasstone and E. J. Riggs.

"Polymerisation of acetone by calcium carbide." By T. Hopkins.

"Action of zinc alkyl halides on nitric esters." By T. Hopkins.

"Observations on the Claisen reaction." By G. T. Morgan and E. Holmes.

"The specific heats of hydrocyanic acid. A reply." By E. H. Ingold.

"The relation of homogeneous to catalysed reactions. The catalytic decomposition of hydrogen iodide on the surface of platinum." By C. N. Hinshelwood and R. E. Burk.

"The action of hydrogen fluoride on compounds of selenium and tellurium. Part II. Tellurium dioxide." By E. B. R. Prideaux and J. O'N. Millott.

"Halogenation of 2 : 6-dimethylbenzbisthiazole and of 2 : 4-diphenyl-3 : 5-diphenyliminotetrahydro-1 : 2 : 4-thiodiazole." By R. F. Hunter.

*

"The reaction between hydroxylamine and ferric chloride." By A. D. Mitchell.

"The equilibria underlying the soap-boiling processes. The system potassium oleate–potassium chloride–water." By J. W. McBain and W. J. Elford.

"The solubility of sodium iodide in ethyl alcohol." By F. E. King and J. R. Partington.

"Iodination in the carbazole series." By S. H. Tucker.

"The chemistry of the caryophyllene series. Part I." G. G. Henderson, J. M. Robertson, and (in part) C. A. Kerr.

"On the Budde effect in bromine. Part I. The photoactive constituent in wet bromine." By B. Lewis and E. K. Rideal.

"On the Budde effect in bromine. Part II. The kinetics of the reaction and the light absorption of wet and dry bromine." By B. Lewis and E. K. Rideal.

"The constitution of the benzene nucleus." By B. C. McEwen.

"Keto-enol isomerism of ethylenebisacetylacetone." By G. T. Morgan and C. J. A. Taylor.

"A buffer mixture for the alkaline range of hydrogen-ion concentration determinations." By W. R. G. Atkins and C. F. A. Pantin.

"The influence of carbon rings on the velocity of reactions involving their side-chains. Part I. The hydrolysis of cyclic and open-chain malonic esters." By R. Gane and C. K. Ingold.

"The condensations of 3-bromo-, and 3-nitro-*p*-dimethylaminobenzaldehydes with ethyl acetoacetate and ammonia." By L. E. Hinkel and W. R. Madel.

"The replacement of calcium carbonate by iron pyrites in nature." By C. O. Harvey.

"A revision of the structural formula of glucose." By W. Charlton, W. N. Haworth, and S. Peat.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE BALLOT TO BE HELD AT THE ORDINARY SCIENTIFIC MEETING ON THURSDAY, DECEMBER 3rd, 1925.

Andrew, Robert Leslie, Dominion Laboratory, Wellington, New Zealand. British (by birth). Analyst. Nineteen years' experience in Dominion Laboratory, N.Z., now senior assistant in charge of Food and Drugs work. Published work: "The Colorimetric Estimation of Lead in Cream of Tartar," *Analyst*, 1924, p. 129. "The Cryoscopic Method for the Detection of Added Water in Milk" (appendix to 50th Annual Report, Dominion Laboratory). (*Signed by*) J. S. Maclaurin, P. W. Robertson, K. M. Griffin.

Baissac, Louis, Curepipe Road, Mauritius (Indian Ocean). British. Sugar Technologist, Department of Agriculture, Réduit, Mauritius. Lecturer

in Sugar Technology, College of Agriculture, Réduit, Mauritius. (*Signed by*) James P. Ogilvie, H. Tempany, W. H. Edwards.

Barker, William Francis, Rhodes University College, Grahamstown, S. Africa. Professor of Chemistry. Ph.D. (Liverpool). (*Signed by*) I. M. Heilbron, E. C. C. Baly, R. A. Morton.

Basden, Ralph, 11, Ada St., Hamilton, Newcastle, N.S.W. Teacher of Chemistry. I have been engaged for four years as Teacher of Science at Sydney Grammar School; two years Teacher of Organic and Physical Chemistry at Newcastle Technical College, and four years in Manufacturing and Analytical Chemistry. (*Signed by*) A. R. Penfold, Robt. Grant, Fred J. Berry, Richard W. Challinor.

Bell, Frank, 11, Edwy Parade, Gloucester. British. Student. Research student at Battersea Polytechnic. (*Signed by*) J. Kenyon, F. C. Ray, Henry Phillips, A. Houssa, Harold Hunter, P. W. B. Harrison, S. Greenberg.

Bennett, Arthur Neville Copnall, 27, Dale Rd., Luton. British. Research Chemist to B. Laporte, Ltd., Luton. B.Sc. (Hons.) London. Have done research under Prof. Donnan at University College, and hope to publish shortly. (*Signed by*) W. E. Garner, D. McKie, Thomas Iredale.

Betts, Harold Frederick, 17, The Broadway, Broadstairs, Kent. British. Research Student, East London College (Univ. of London). B.Sc. (Lond.), 2nd Class Hons. Chemistry. (*Signed by*) J. R. Partington, D. C. Jones, E. E. Turner.

Bird, John Cecil, 72, Dyne Rd., Kilburn, London, N.W. 6. British. Research and Works Chemist. B.Sc. (London), A.I.C., Associate of Univ. College of Nottingham. Science Master, Grammar School, Daventry. Chemist to Messrs. L. B. Holliday & Co., Ltd., Huddersfield. Chief Chemist and Works Manager to J. W. Drysdale & Co., London. Chemist to Messrs. Intermediates and Explosives, Ltd. (Bolckow, Vaughan & Co.), Co. Durham. Chemist to Messrs. Crookes Laboratories (British Colloids, Ltd., London). Investigation with Prof. H. H. Hodgson, M.A., into Absorption Spectra of Standard Dyestuffs (Huddersfield). (*Signed by*) Herbert Henry Hodgson, F. S. Kipping, E. R. Trotman.

Birkett, Lionel Christopher William, Moor House, North Rd., Spennymoor, Co. Durham. British. Analytical Chemist on Coke Oven and Bye-products Plant. 5½ years' experience in Ironworks and Coke Oven laboratories. B.Sc. (3rd Class Hons.) after 3 years' study at Armstrong College, Newcastle-on-Tyne. (*Signed by*) W. N. Haworth, G. C. Leitch, H. V. A. Briscoe.

Boyd, James, P.O. Box 1162, Johannesburg, S. Africa. British. Chief Examiner of Mine Air, Chamber of Mines, Johannesburg (and Assistant to General Manager, Chamber of Mines). F.I.C., A.R.T.C. (Glasgow). Assistant to Professor of Chemistry, Royal Technical College, Glasgow, 1908–11. Chemist, Goldfields Lab., Transvaal, 1912–13. Chief Examiner of Mine Air, Chamber of Mines, Johannesburg, 1914 to date. Author of various reports on Dust in Mine Air and Methods of investigating same (published in "Chamber of Mines Annual Reports," and for circulation to the mines of the Rand). Student, Royal Technical College, Glasgow, 1904–08. (*Signed by*) G. G. Henderson, Thomas Gray, F. J. Wilson.

Bradhurst, Frank Symonds, Bondi, Sydney, and c/o Holbrooks Ltd., Danks St., Waterloo, Sydney. Chief Chemist and Factory Manager. Matriculated from Sydney High School at Leaving Certificate Examination; obtained Scholarship available at the Sydney Technical College. Here I obtained the Honours Diploma with College Medal for year in Organic Chemistry, thereby becoming an Associate of the Sydney Technical College (A.S.T.C. Chem.).

Associate of the Australian Chemical Institute (A.A.C.I.). Chemist at Stedman-Hendersons, Ltd., Sweet Manufacturers, for 2½ years, then at Holbrooks (Australasia), Ltd., of Sydney, for 3 years, where I now hold the above position. I desire admission to the Chemical Society in order to keep in touch with modern research in the field of Food Analysis, and Food Manufacture. (*Signed by*) Richard W. Challinor, Fred J. Berry, Robert Grant, Arthur R. Penfold, S. E. Sibley.

Britnell, Edward, 9, Osterley Av., Isleworth, Middlesex. English. Chemist. B.Sc. (Honours Chemistry), London, July 1925. Assistant for 3 years to G. N. Huntly, 325, Kennington Rd., S.E. Assistant for 1½ years to G. T. Holloway & Co., 13, Emmett St., Limehouse. (*Signed by*) William G. Wagner, G. Nevill Huntly, Herbert F. Stephenson.

Bromfield, Reginald John, 141, Constantine Rd., Hampstead, N.W. 3. English. Assistant to Biochemist, The Hospital for Sick Children, Great Ormond St., W.C. For three years laboratory assistant at University College, London, under Prof. F. G. Donnan and Prof. N. Collie. For one year Acting Biochemist to Children's Hospital, Gt. Ormond St. For past two years Biochemical assistant, Hospital for Sick Children, Great Ormond St. Desire to become a member in order to receive the Journal and to keep in touch with current chemical literature, together with access to Library. (*Signed by*) J. N. Collie, Henry Terrey, Fred J. Kettel, J. Wicliffe Peck.

Burstall, Francis Hereward, 12, Adelaide Road, Teddington, Middlesex. British. Research Chemist. D.S.I.R. Chemical Research Laboratory, Teddington. 1st Class Honours B.Sc., Birmingham University. (*Signed by*) G. T. Morgan, E. Holmes, C. E. Wood.

Butterfield, Archer John William, 163, Northumberland Park, Tottenham, N. 17. English. Articled Pupil in Engineering. Is desirous of keeping in touch with progress in the Science of Chemistry by attending the meetings and receiving the publications of the Society. (*Signed by*) W. J. A. Butterfield, Ernest M. Hawkins, E. R. Bolton.

Carlile, John Hildred George, 29, Orlando Rd., Clapham, S.W. 4. British. Chemical Research Student, Royal College of Science. A.R.C.Sc., B.Sc. (*Signed by*) H. J. T. Ellingham, James C. Philip, H. F. Harwood.

Chalk, Leslie James, 14, Shrubbery Rd., Southall, Middx. Student (East London College). B.Sc., 1st Class Hons. in Chemistry. J. R. Partington, E. E. Turner, Elwyn Roberts.

Charan, Rama, Allahabad, India. Indian (British). Glass Technologist. Govt. of India State Technical Scholar, B.Sc. from Allahabad University, 1922. Subjects: Maths., Physics, Chemistry, and English. B.Sc. Tech. from Sheffield University, 1924. Subjects: Glass Technology, Fuel, Refractory Materials, Geology and Mineralogy of Glassmaking Materials. For one year after graduation did research work on glasses containing more than one alkaline oxide and silica-lime. (*Signed by*) W. E. S. Turner, C. J. Peddle, F. G. Tryhorn.

Corran, John William, Research Laboratory, Carrow Works, Norwich. British. Physical and Biochemist. B.Sc. (Liv.), 1st Class Hons. Chem., 1921; Ph.D. (Liv.), 1923; A.I.C. Two years Research Physical Chemistry under Prof. W. C. M. Lewis; two years as physical and biochemist to Liverpool Cancer Research Committee. Publications: *J. Amer. Chem. Soc.*, 1922, **44**, 1673; 1923, **45**, 1627. *Biochem. J.*, 1924, **18**, 1358, 1364. (*Signed by*) W. C. M. Lewis, E. C. C. Baly, E. Morrison, Leslie J. Harris.

Cottier, John Harold, 52, Aspen Grove, Lodge Lane, Liverpool. British. Certificated School-teacher; formerly a student of Sheffield University. I

wish to obtain the Fellowship of the Society in order to receive the Journal and Abstracts, and thus keep in touch with advances in Chemistry. (*Signed by*) W. P. Wynne, F. G. Tryhorn, E. G. Turner, D. M. Bennett.

Crowther, Edward Mortimer, Rothamsted Exptl. Station, and Bourtree, 24, Clarence Road, Harpenden, Herts. British. Assistant Physical Chemist and "Empire Cotton Growing Corporation," Soil Physicist, Rothamsted Exptl. Station. D.Sc. (Leeds), F.I.C., A.Inst.P. Publications on Physical Chemistry of Soils. *Journ. Agric. Sci.*, 1925, **15**, 201–255, 300–302, 303–306; *Trans. Faraday Soc.*, 1922, **17**, 317–321. Conjointly: *Journ. Agric. Sci.*, 1924, **14**, 221–231; 1925, **15**, 68–88; *Proc. Royal Soc.*, 1925, **106A**, 33–51, 215–222, 233–242; *Annals of Applied Biology*, 1925, **12**, 152–190. (*Signed by*) E. J. Russell, H. J. Page, C. T. Gimingham.

Dickinson, Frank Edwin, Research Establishment, Sutton Oak, St. Helens, Lancs. British. A/g Superintendent, The Research Establishment, Sutton Oak, St. Helens, Lancs. Actively engaged in Chemical Industry as Analytical and Research Chemist and as Assistant Manager and Manager of Chemical Works for past fourteen years. Educated at King Edward's School, Stratford-on-Avon, and University of Birmingham. No papers published as all work of secret nature or commercial value. (*Signed by*) J. Davidson Pratt, E. Wheeler, Francis H. Carr.

Dolphin, Joseph Raymond, Chemical Department, University Rd., Edgbaston, Birmingham. British. Research Student. Pass B.Sc. Birmingham, 1st Class, 1923; Honours B.Sc. Birmingham, 1st Class, 1924. Research Student under Professor Morgan, O.B.E., D.Sc., F.R.S., from 1924–25 to become Research Chemist at J. A. Crabtree & Co., Ltd., Walsall, in Sept. 1925. (*Signed by*) G. T. Morgan, C. E. Wood, E. Ashley Cooper.

Donovan, William, Dominion Laboratory, Wellington, New Zealand. British. Analyst, Dominion Laboratory, N.Z. M.Sc. (New Zealand University). Twenty years' experience in analytical work; now Assistant Dominion Analyst. Published work includes "Corrosion of Muntz Metal in Sea Water," *J.S.C.I.*, XLIII, 13, 72T; "Estimation of Nitrogen in Coal," *The Analyst*, Feb. 1924. (*Signed by*) J. S. Maclaurin, P. W. Robertson, K. M. Griffin.

Dunn, John Stanley, 39, Victoria Park, Cambridge. British. Chemist. M.A. (Cantab.), Ph.D. (London), A.I.C. Late Research Chemist, Calico Printers Assocn., Manchester; now Research Chemist, British Non-Ferrous Metals Res. Assocn. With Dr. E. K. Rideal: *T.*, 1923, **123**, 1242; *T.*, 1924, **125**, 676. (*Signed by*) R. G. W. Norrish, Eric K. Rideal, H. McCombie.

Dyde, John Horsfall, 18, Dean Rd., Scarborough. British. Student at the University, Leeds, who intends to pursue post-graduate work in Biochemistry. Final year B.Sc. (Honours Chemistry). (*Signed by*) C. K. Ingold, B. Topley, H. M. Dawson.

Dyson, George Malcolm, 36, Hillsborough Road, E. Dulwich, London, S.E. 22. British. Research Chemist. B.A. (Oxon.), B.Sc., Ph.D. (London). Research in Organic Chemistry, including work on the Reactions of Thiocarbonyl Chloride with Amino-compounds, Phenols, etc. *J.C.S.*, Trans., Sept., 1924, **125**, 1702; "The Reactions of Thiocarbonyl Chloride. Pt. I." (*Signed by*) D. L. Chapman, H. J. George, L. Rubenstein.

Eccles, Alfred, 18, Cambrian Terrace, Holbeck, Leeds. British. Research Student (University of Leeds). B.Sc., 1st Class Hons. (Pure Chemistry), 1925. (*Signed by*) C. K. Ingold, P. K. Dutt, W. A. Wightman, J. W. Baker.

Edwards, Edwin Francis, Kogarah, Sydney, N.S.W., c/o Holbrooks (Australasia), Limited, Waterloo, Sydney. Works Chemist and Assistant

Factory Manager. Matriculated from High School at Leaving Certificate Examination, and gained Scholarship to Sydney Technical College. Attended the above College for five years—thereby completing the Diploma Course—and was subsequently granted the Associateship of the College, and the Diploma in Organic Chemistry. I am also an Associate of the Australian Chemical Institute. I was Assistant Chemist at the Woolwich Chemical Co., Sydney, for a period of two years, and Analyst at H.M. Customs, Sydney, for twelve months. At present I hold the above-mentioned position on the Staff of Holbrooks (Australasia), Limited, of Sydney. I desire admission to the Chemical Society in order to keep in touch with modern chemical literature and progress. (*Signed by*) Richard W. Challinor, Fred J. Berry, Robert Grant, Arthur R. Penfold, S. E. Sibley.

Edwards, John Moelwyn, 92, Jamaica Rd., Rotherhithe, S.E. 16. British. Chemist and Pharmacist and Optician. (1) Early education at the Meirioneth County Grammar School. (2) Three years student of Chemistry at the Festiniog Higher Grade School. (3) Studied Analytical Chemistry and Physics under Mr. J. Thomas, B.Sc., at Muter's School of Chemistry. (4) Passed the Qualifying Examination of the Pharmaceutical Society of Great Britain in 1905. (5) Four years Sight Testing Optician with Mr. Hugh Jones, F.S.M.C., D.B.O.A. Am particularly anxious to keep in touch with Analytical work. (*Signed by*) Frank B. Arnold, John J. Laws, Percy Barrs.

Elliott, George Albert, 263, Kennington Road, London, S.E. 11. British. Ramsay Memorial Fellow. M.Sc. (Lond.). (*Signed by*) L. F. Gilbert, S. Barratt, W. E. Garner.

Evans, Eric Bertram, 2, Boxmoor Terrace, Southchurch, Southend, Essex. English. Student. For two years a student at East London College; at present engaged in research there. Awarded 2nd Class in B.Sc. Hons. Lond., 1925. (*Signed by*) J. R. Partington, E. E. Turner, Elwyn Roberts.

Ewbank, (Miss) Elinor Katharine, 22, Park Crescent, Oxford. British. Engaged in original research. Took 1st Class in Honours, School of Chemistry, Oxford, 1903. E. C. C. Baly and E. K. E., **87**, 1347; **87**, 1355. N. V. Sidgwick and E. K. E., **119**, 486; **121**, 1844; **125**, 2268. (*Signed by*) W. H. Perkin, N. V. Sidgwick, D. Ll. Hammick.

Farrow, (Miss) Elizabeth Monica Openshaw, 37, Chalfont Rd., Oxford. British. Demonstrator in Old Chemistry Dept., Oxford. Lecturer in Chemistry to 5 Women's Societies. M.A. (Oxon.) (*Signed by*) W. H. Perkin, N. V. Sidgwick, B. Lambert, M. P. Applebey, Allan F. Walden, E. G. J. Hartley, Frederick Soddy, J. Masson Gulland, S. G. P. Plant.

Free, Oliver, The Lodge, Mansfield College, Oxford. British. Demonstrator of Inorganic Chemistry. B.A., 2nd Class Honours. Research Student in Physical Chemistry (Radioactivity). (*Signed by*) M. P. Applebey, Frederick Soddy, B. Lambert, N. V. Sidgwick, A. F. Walden.

Freeman, William Marshall, 16, Oakwood Avenue, Beckenham, Kent. British. Of the Honourable Society of the Middle Temple, Barrister-at-Law, Recorder of Stamford, and formerly Member of the Pharmaceutical Society of Gt. Britain. Author of "The Patents and Designs Act 1907, with Appendix on Chemical Patents." Occasional contributor to legal and other journals on Food and Drugs legislation, etc. Interested particularly in the promotion of the study of chemico-legal science especially with reference to the administration of the criminal law. (*Signed by*) Ernest C. Bennison, H. Berry, Harry Silvester.

Gee, Eva Florence, The Station, L.N.E.R., Howsham, Lincoln. British.

Student of Chemistry at Bedford College. (*Signed by*) J. F. Spencer, H. Crompton, J. Stewart.

Gemmell, James Walter Shanks, Helen's Villa, Fleming Place, St. Andrews. British. Research Chemist. B.Sc. (Hons.) St. Andrews; now employed in Research Dept., Jute Industries, Ltd., Dundee, and desirous of keeping in touch with recent developments in chemical science. (*Signed by*) A. Killen Macbeth, James Craik, John Pryde.

Glover, Francis Reginald, 98/100, St. Peter's Street, Nottingham. British. Managing Director, Cooke & Glover, Engineers, Ltd., Engineers and Consulting Chemists, Nottingham, M.I.H.V.E., A.M.I.S.E. (*Signed by*) E. B. R. Prideaux, J. B. Firth, B. D. Shaw.

Goudielock, William Bouch O'Brien, 28, Fairfield Lane, Barrow-in-Furness. British. Chief Analyst, Vickers Ltd., Barrow-in-Furness. Full Technological Certificate, City and Guilds Institute, in Chemistry, Metallurgy, and Iron and Steel. Pupil in Vickers' Lab. under H. B. Weeks, F.I.C., for 5 years. Chief Laboratory Assistant for 8 years. Chief Analyst ever since. Lecturer for 2 years to Vickers' Engineering Apprentices on Chemical and Metallurgical Subjects in Connection with Firm's Scheme for Higher Education of Apprentices. Lecturer to Barrow Engineer's Assoc., Jan. 1920 and Jan. 1923. I am desirous of keeping in close touch with modern developments in Scientific Chemistry. (*Signed by*) H. B. Weeks, A. H. Mundey, W. J. Davison.

Grigg, Felix John Theodore, Christchurch (N.Z.). British. Government Analyst, Government Buildings, Christchurch, N.Z. M.Sc. (N.Z.) with Honours in Chemistry. A.I.C. (Great Britain). Seven years' experience in analytical work. Now Government Analyst at Christchurch (N.Z.). Published work: "Geochemistry of the Thermal Lakes, North Island, N.Z." (*N.Z. Journal of Science and Technology*, 1922, Volume 5, page 156). (*Signed by*) J. S. Maclaurin, P. W. Robertson, K. M. Griffin.

Hall, George Vincent, 6, Borough Road, Bridlington, Yorks. British. Student. Bachelor of Science, University of Leeds, June 1925. (*Signed by*) C. K. Ingold, H. M. Dawson, W. Lowson, P. K. Dutt.

Hall, John, 202, Burton Rd., Derby. British. Chemist. M.Sc. (Leeds), A.I.C. Three years in Lab. of Sir W. G. Armstrong-Whitworth & Co.; two years in Lab. Dyehouse and Colour Plant of British Celanese. *J.C.S.*, **123**, 2029–2037. (*Signed by*) A. G. Perkin, G. Reeves, W. P. Skertchly.

Hare, William Rowan, 220, Eastfield, Peterborough. British. Student of Chemistry in the University of Oxford. Desirous of receiving literature (*Signed by*) D. Ll. Hammick, S. G. P. Plant, E. Hope.

Healey, Walter, 28, Gooder Lane, Brighouse. English. Student, University of Leeds. Chemical Student who hopes to take up research. (*Signed by*) C. K. Ingold, P. K. Dutt, W. A. Wightman.

Henderson, Thomas, M.C., M.A., B.Sc., Toronhill Schoolhouse, Dunfermline. Scottish. Demonstrator in Chemistry (Inorganic), University of Leeds. M.A., B.Sc., St. Andrews, 1921. Holding a grant from the Dept. of Scientific and Industrial Research, carried on research work at St. Andrews University, under direction of Sir James C. Irvine, and have held the appointment noted above since October 1922. Vol. **121**, 1922, Trans., p. 892; Vol. **123**, 1923, Trans., p. 1130. (*Signed by*) R. Whytlaw-Gray, H. S. Patterson, B. Topley, W. Lowson, J. C. Irvine, Ettie S. Steele.

Hirst, Herbert Sim, Trinity College, Cambridge. British. Research Assistant to Dr. E. K. Rideal, under Department of Scientific and Industrial Research Regulations. First class honours graduate in Physics and Chemistry

of St. Andrews University, with two years' research experience in Cambridge. "The Thermal Decomposition of Nitrogen Pentoxide," 1925, **127**, 657. (*Signed by*) Eric K. Rideal, W. H. Mills, Ulick R. Evans.

Husain, Syed, 112, Gower St., London, W.C. 1. Indian. Student. M.Sc. (Aligarh Muslim University, India). (*Signed by*) J. R. Partington, E. E. Turner, Elwyn Roberts.

Iwadare, Toru, c/o Banyu Pharmaceutical Co., Ltd., 174, Shimomeguro, Tokyo, Japan. Japanese Proper. Became Chief Chemist and Managing Director of Banyu Pharmaceutical Co., Ltd., in September 1915. Have two years' experience as Assistant of the Chemical Dept. of the Tokyo Imperial University, and ten years' experience as Chief Chemist and Managing Director of Banyu Pharmaceutical Co., Ltd. Graduate, College of Science (Chemistry), Tokyo Imperial University, 1913. (*Signed by*) Joji Sakurai, T. Takamatsu, Y. Asahina.

Jayewardene, David Christopher Mendis, Fern Bank, Moratuwa, Ceylon. Sinhalese, British. Science Master, Prince of Wales' College, Moratuwa. (1) Science Master, St. John's College, Panadura, Ceylon (1918 and 1919). (2) Asst. Chemist, Butter Substitutes Supplies, Ltd., Colombo (1920). (3) Science Master, Prince of Wales' College, Moratuwa (since 1921). (*Signed by*) W. N. Rae, J. P. C. Chandrasena, K. V. Rau.

Jessop, Gilbert, 453, Glossop Rd., Sheffield. British. Research Chemist. M.Sc., Ph.D. (Sheffield). Three years' Research in Physical Chemistry. Papers in the *Proc. Roy. Soc.*, 1925, **98B**, 206 (with Mr. N. K. Adam), and in the *J.C.S.* (with Mr. F. G. Tryhorn), 1925, **127**, 1320; (with Mr. N. K. Adam), 1925, **127**, 1863. (*Signed by*) W. P. Wynne, F. G. Tryhorn, N. K. Adam.

Johnson, Charles Benjamin, 134, Preston New Road, Blackburn. British. Minister of Religion (Fellow of Royal Astronomical Society). I desire to keep abreast, by means of the Society's Publications, of advance in General and Physical Chemistry. (*Signed by*) G. W. F. Holroyd, J. Hindle, Robert H. Pickard.

Jones, Walter Idris, 7, Manor Street, Cambridge. Welsh. Research Student. Gonville and Caius College, Cambridge. Ph.D. (Cantab.), B.Sc. (Wales), etc. *Trans. Chem. Soc.*, 1923, **123**, 2688; 1924, **125**, 2590. (*Signed by*) Hamilton McCombie, John Dexter, Harold A. Scarborough.

Keenan, Henry Wilfrid, 80, Upper Richmond Road, East Sheen, S.W. 14. British. Works Chemist. Practical experience in various branches of Analytical and Manufacturing Chemistry founded on a three years' Systematic Apprenticeship (with evening studies) under Dr. Julius Holzapfel and Dr. P. E. Bowles, F.I.C., by whom indentures are signed. Invented processes (including design and erection of plant for large scale production) dealing with (*a*) Paint and Varnish Industry, (*b*) Celluloid Industry, (*c*) Oils, and operated successfully. (*Signed by*) Charles Dorée, Francis Arnall, J. C. Crocker.

Kemp, Brian Charles Lavers, Wellington College, Berks. British. Schoolmaster. Chemistry Master (VIth Form) at Wellington College; B.A. (Oxon.). 1922–23, research work on derivatives of Dianisoyl Methane. (*Signed by*) G. Watson Gray, D. Ll. Hammick, B. Lambert.

King, Charles, F.S.A. (Scot.), 21, Newton Place, Glasgow. British. Electro-therapeutist. Fellow of the Society of Science, Lond. Applicant is in practice as Electro-therapeutist, and is desirous of keeping in touch with current chemical progress. (*Signed by*) G. G. Henderson, J. Roberts, Archd. N. Currie.

Koch, Frederick Karl Victor, 9, Crossfield Road, Hampstead, N.W. 3.

English. Research in Physical Chemistry, Imperial College of Science and Technology. B.Sc. (1st Class), A.R.C.S. (2nd Class). (*Signed by*) James C. Philip, H. J. T. Ellingham, H. F. Harwood.

Langford, Charles Dudley, 43, Ashbourne Av., Temple Fortune, London, N.W. 11. British. Research Student (Organic Chemistry), Royal College of Science. A.R.C.S., B.Sc. Honours (passed 1925, to be awarded 1926 owing to regulations). (*Signed by*) G. A. R. Kon, R. W. West, E. H. Farmer.

Laroia, Banarsi Das, Pindi Street, Ludhiana, Punjab, India. Indian. Student. B.Sc. (Hons.) Punjab University (India), B.A. (Hons.) Oxford University. At present student of Imperial College of Science and Technology (for Ph.D.). (*Signed by*) E. H. Farmer, G. A. R. Kon, M. A. Whiteley.

Laszlo, Henry Guinness de, 3, Fitzjohn's Avenue, Hampstead, N.W. 3. British. Research Chemist. B.A. Hons. (Cantab.), Ph.D. (Zurich). (*Signed by*) M. A. Whiteley, G. Ingle Finch, Samuel Smiles.

Leatherbarrow, Bertram Grey, Hill Crest, Station Rd., Brimington, Chesterfield. British. Senior Assistant Teacher, Brimington Central School. Intermediate B.Sc. Two years subsequent graduation courses. Headmaster, Brimington Central Evening School, teaching all the Technical Courses. Student, Liverpool University 1919–1923. (*Signed by*) E. C. C. Baly, W. C. McC. Lewis, I. M. Heilbron, H. J. Stern.

Lenher, Sam, 15, Gordon Street, London, W.C. 1. American. Research Student at the Ramsay Laboratory, University College, London. Graduate of the University of Wisconsin (B.A. Degree), 1924. Internal student for the Ph.D. degree, University College, London, one year. McHaffie and Lenher, *J.C.S.*, 1925, **127**, 1559—1572. (*Signed by*) F. G. Donnan, W. E. Garner, J. A. Currie.

Lennon, John Joseph, 6, Bartlemas Road, Oxford. Irish. Research Student. M.Sc., National University of Ireland, 1924, 1851 Scholar. Paper in collaboration with Hugh Ryan, D.Sc., *Proc. Royal Irish Acad.*, xxxvii, B, p. 27. (*Signed by*) W. H. Perkin, Francis Lions, R. D. Haworth, John Rankin.

Macartney, William, c/o Grattan & Co., Ltd., Belfast. British. Pharmaceutical Chemist. Chief Chemist of Messrs. Grattan & Co., Ltd., Wholesale Manufacturing Chemists and Aerated Water Manufacturers. Member of the Pharmaceutical Society of Ireland. Vice-President North Irish Pharmaceutical Society, Vice-President Ulster Drug Trade Association. No published papers in the *Journal of the Chemical Society*. In order to keep in touch with current advances in Chemistry. (*Signed by*) Henry Wren, Chas. J. Still, A. W. Stewart, Theo. Harper.

McHaffie, Ivan Roy, 37, King Henry's Rd., London, N.W. 3. Canadian. Research Student, University College, London. B.A., M.Sc. University of Manitoba, Canada. "The Adsorption of Water from the Gas Phase on Plane Surfaces of Glass and Platinum," *J.C.S.*, 1925, **127**, 1559–1572. (*Signed by*) F. G. Donnan, W. E. Garner, S. Barratt.

McLean, Neil, M.A., B.Sc., 127, Blenheim Place, Aberdeen. British. Station Director of the British Broadcasting Station at Aberdeen. Applicant is a Master of Arts and Bachelor of Science of Glasgow University, and is much interested in chemical science and desirous of having the best available literature on this subject for the purposes of his work. (*Signed by*) J. F. Tocher, G. G. Henderson, Archd. N. Currie.

Manchester, Leslie George, 557, Green Lanes, Hornsey, N. 8. British. Student. Two years a student at East London College; now engaged in

research work at same college; awarded 2nd Class in B.Sc. Hons. Lond. 1925. (*Signed by*) J. R. Partington, E. E. Turner, R. J. W. Le Fèvre.

Markwell, William Alfred Nottage, 26, Huntsmoor Road, S.W. 18. English. Chemist. Desire to receive the *Journal* and to keep in touch with the progress of Chemical Science. (*Signed by*) E. W. Lucas, S. Greenberg, F. C. Ray, J. L. White, Henry Phillips.

Martin, William Francis, 27, Shandon Crescent, Edinburgh. British. Work's Chemist, in the employment of Messrs. T. & H. Smith, Ltd., Blandfield Chemical Works, Edinburgh. Fellow of Institute of Chemistry (F.I.C.), Member of Pharmaceutical Soc. of Gt. Britain (M.P.S.). (*Signed by*) James Walker, Alexander J. Dey, James Watt.

Miller, Charles Henry Lawrence, 50, Rowden Rd., Beckenham, Kent. British. Student (B.Sc. Honours Chemistry) at East London College. At present doing research work. Desirous of keeping in touch with modern Chemical Research. (*Signed by*) J. R. Partington, E. E. Turner, D. C. Jones, W. H. Patterson.

Moore, Arthur, Highfield, Oakworth, Keighley, Yorks. British. Student (Chemistry). 3rd Year (final) Hons. Chemistry, Royal Coll. of Science, London, S.W. 7. (*Signed by*) H. L. Riley, H. F. Harwood, H. D. Murray.

Morrison, Alexander John, Sydney, N.S.W. Assistant Superintendent of Testing and Inspection, Public Works Dept., Sydney. *Training :* Student for 3 years (night course) in the Chemical and Assay Laboratory of the late William Grosse, Mining Engineer and Metallurgist. *Sydney Technical College :* 4 years' course practical chemistry; 3 years' course theoretical chemistry; 2 years' course organic chemistry. Engaged on special investigation in connection with fixed oils and alloys. *Original Papers :* (With F. R. Morrison), "Examination of the fixed oil of the Queensland Nut," read before the Sydney Technical College Chemical Society (Vol. 1, pages 84—88). "Testing of Sand for Use in Portland Cement Mixtures," Paper read before the Sydney Technical College Chemical Society 1914 (Vol. 1, pages 17—26). "Permeability of Concrete" (with the late B. J. Smart, B.Sc. (London), Paper read before the Engineering Association of New South Wales (Vol. xxxiii, Part 2, page 1). Have been engaged in the chemical and mechanical testing of all classes of structural materials in the Testing Laboratory, Public Works Department, New South Wales, for the past 27 years. These materials include Portland cement, steel, alloys, asphaltum, tars, paints, oils, etc. Representative of the Australian Chem. Institute on the Engineering Standardisation Committee dealing with the drawing up of a Standard Specification for Portland Cement for the Commonwealth of Australia. (*Signed by*) A. R. Penfold, R. Grant, Richard W. Challinor, Fred J. Berry, George Z. Du Pain.

Morrison, Frank Richard, Brae Street, Waverley, Sydney, N.S.W. Australia. Asst. Economic Chemist, Technological Museum, Sydney. Diploma in Chemistry of Sydney Technical College, 1921. Associate of Australian Chemical Institute since 1920. Member of Royal Society of N.S.W. since 1921. Member of Sydney Technical College Chemical Society since 1913, and Joint Hon. Secretary since 1921. *Positions held :* One year in laboratory of Sydney Technical College; three years in laboratory of Metropolitan Board of Water Supply and Sewerage, Sydney; nine years in present position at Technological Museum, Sydney. *Original papers :* "The Occurrence of Rutin in the leaves of the *Boronia* (N. O. Rutaceæ)" (read before the Royal Society of N.S.W., 2nd November, 1921); "The

essential oil of *Kunzea corifolia*" (read before the Royal Society of N.S.W., 1st November, 1922); "A Chemical examination of the seeds of the 'Bunya Bunya' (*Araucaria Bidwilli*, Hooker)" (read before the Royal Society of N.S.W., 3rd December, 1924). *Conjointly with Mr. A. R. Penfold, F.A.C.I., F.C.S.* "Preliminary note on a new stearoptene (probably a phenol ether) occurring in some essential oils of the Myrtaceæ" (read before the Royal Society of N.S.W., 5th July, 1922); "The essential oil of *Eriostemon Crowei* (*Crowea saligna*) and the presence of a new phenol ether" (read before the Royal Society of N.S.W., 6th December, 1922); "Preliminary note on the electrolytic reduction of Piperitone" (read before the Royal Society of N.S.W., 5th September, 1923); "Notes on *Eucalyptus piperita* and its essential oils, with special reference to their Piperitone content" (read before the Royal Society of N.S.W., 2nd July, 1924). *Conjointly with Mr. A. Morrison:* "The chemical examination of the fixed oil of the Queensland Nut (*Macadamia ternifolia*)" (read before the Sydney Technical College Chemical Society, 24th June, 1923). (*Signed by*) A. R. Penfold, R. Grant, Richard W. Challinor, Fred J. Berry, George Z. Du Pain.

Murgatroyd, John Blackburn, 90, St. George's Square, Westminster, S.W. 1. British. Demonstrator, Imperial College of Science and Technology, South Kensington. Taking up Research at the above College. (*Signed by*) H. B. Baker, J. N. Sugden, Leslie S. Theobald.

Nanavati, Chitsukhlal Hiralal, 80, Esplanade Road, Fort, Bombay. Hindoo. L.T.C., Analytical Chemist. Graduate of The Victoria Jubilee Technical Institute, Bombay; in Chemistry with special subject of Foods, Drugs and General Analysis; in Second Class with the title of Licentiate of Technical Chemistry, of the year 1921. Worked as Analytical Chemist with Messrs. Hughes & Davies and Messrs. Killick, Nixon & Co.; at present practising as Analytical Chemist. (*Signed by*) S. J. Shàh, Kapilram H. Vakil, R. G. Saraiya.

Nicholson, Henry, "Aberlady," Osborne Rd., Stockton-on-Tees. English. Chemistry Master in Boys Secondary School, Stockton-on-Tees, since Nov. 1905. B.Sc. Durham University, 1904. M.Sc. for Research on the influence of the acetyl group as a protective agent in the oxidation of α-acetylnaphthylamine, 1907. (*Signed by*) J. G. Taylor, J. A. Smythe, W. M. Madgin.

O'Meara, Anna Maria, 83, Elsham Road, Holland Park, Kensington, W. 14. Irish. Pharmacist. M.P.S. (London). Was for 4 years trained under John Armstedt Ray, M.A., Ph.C., Trinity Coll., Dublin, at his Laboratory in 23, Nassau Street, but never took any Analytical Examination. Was 3 years Pharmacist at Bolingbroke Hospital, Wandsworth Common, S.W. 11; was 1 year at Willesden General Hospital as Pharmacist, and occasionally have worked at the M.A.B. Homerton and Park Royal, Hither Green. At present am pharmacist at the Women's Hospital, Soho Sq., and I take Students for both the qualifying and Apothecaries' Hall Exam. and train them for same. (*Signed by*) H. Lucas, A. Thomas, S. Greenberg.

Palmer, Horace Winston, 15, Hollingdean Terrace, Brighton. British. Research Student, East London College. B.Sc. London, Hons. I, Chemistry. (*Signed by*) J. R. Partington, D. C. Jones, W. H. Patterson.

Parker, Norman Frederick, 45, Sellons Avenue, Harlesden, N.W. 10. British (English). Chemical Engineer. B.A. Cambridge; Associate of Institute of Chemistry; 1st Class, Natural Science Tripos, Part II (Chemistry), 1923. (*Signed by*) W. J. Pope, C. T. Heycock, W. H. Mills.

Patterson, Austin McDowell, Antioch College, Yellow Springs, Ohio,

U.S.A. United States. Professor of Chemistry, Antioch College, U.S.A. Formerly Editor of *Chemical Abstracts*. (*Signed by*) C. S. Gibson, T. Slater Price, John Greenaway.

Phillis, Ernest, 22, Fairford Terrace, Dewsbury Rd., Leeds. British. Research Student, Leeds University. B.Sc., 1st Class Hons. in Pure Chemistry, 1925. (*Signed by*) J. B. Cohen, C. K. Ingold, P. K. Dutt, J. W. Baker.

Pollitt, Jonathan, 17, Caversham Avenue, Palmers Green, N. 13. English. Chemistry Master, Hornsey County School, 1905– . B.A. (N.U.I.) Chemistry, Physics, Maths. Student (Chemistry) Birkbeck College since 1908. (*Signed by*) George Senter, Samuel Sugden, B. R. Heasman, F. J. Thorneycroft, A. M. Ward, Wm. W. Myddleton.

Porter, Charles Raymond, 126, Linden Road, Bournville, Birmingham. English. Chemistry research assistant. M.Sc., A.I.C. Three years research assistant in Chemistry Department, University of Birmingham; part author of *Berichte*, 1925, **58**, 333, and *J.C.S.*, 1924, **125**, 731 and 1269. (*Signed by*) J. D. Main Smith, W. J. Hickinbottom, W. N. Haworth.

Price, Evan Emrys, Rock House, Heathfield, Swansea, Glam. British. Science Teacher, The College, Penarth, S. Wales. Graduate in Chemistry of University of Wales. Studied at University College, Swansea, 1920—1924. (*Signed by*) J. E. Coates, Leonard E. Hinkel, E. Stanley Hiscocks.

Pring, Marjorie Ellen, 66, St. Augustine's Avenue, S. Croydon, Surrey. British. Research Student at Bedford College for Women, Regent's Park. B.Sc., 1st Class Hons. in Chemistry, London University. (*Signed by*) J. F. Spencer, H. Crompton, M. S. Crewdson.

Rây, Jnanendra Nath, Calcutta. Indian. Lecturer, Calcutta University, M.Sc. (Cal.). Research Student, Manchester Univ. "Synthesis of oxyberberine" (joint author), *J.*, 1925, **127**, 740; "Synthesis in the Thianthren series," *J.*, 1921, **119**, 1959; "Catalytic action of Iodine in sulphonation," *J.*, 1920, **117**, 1405; joint author, "Modification and extension of Friedel & Crafts' reaction," *J.*, 1920, **117**, 1335. (*Signed by*) Robert Robinson, Arthur Lapworth, Henry Stephen, Wilson Baker.

Roberts, Herbert Charles, 15, Estcourt Terrace, Headingley, Leeds. British. Chemist Director, Taylor's Drug Co., Ltd., P.O. Box 141, Burley Hill, Leeds. 20 years Analytical Chemist to above Co. Since 1908 Chemist Director and Superintendent under the Pharmacy Act to above Co. (*Signed by*) John Rennie, F. C. Savage, F. Pilkington Sargeant.

Sanderson, Phyllis Mary, 7, Cresswell Place, S.W. 10. British. Research (Biochemical). I desire to become a member of this Society for the purpose of keeping in touch with current scientific investigations. (*Signed by*) F. G. Donnan, W. E. Garner, Henry Terrey.

Sass, Rose Rachel, Newnham College, Cambridge. British. Research Student. B.Sc. Hons. of the University of the Witwatersrand, Johannesburg, S. Africa. Demonstrator for 3 years. Now a research student in the Laboratory of Physical Chemistry, Cambridge University. (*Signed by*) T. M. Lowry, Eric K. Rideal, I. J. Faulkner.

Saxon, Robert, Westfield Terrace, Baildon, Yorks. British. Schoolmaster. Teacher of Chemistry at the Belle Vue Secondary School for 17 years. Teacher of Steam and Heat Engines, which included the Thermal Chemistry of Carbon and Hydrogen combustion and tests for SH_2, NH_3, etc., in Coal and Producer Gas for 15 years in the Belle Vue Technical School (evening). Eleven years Head Master present School, The Forster School for Boys, Bradford, under the Bradford Authority; entrance to school only by

Scholarship Examination. Bachelor of Science, Victoria Univ., Manchester, 1896. Studies under Prof. Tilden, Royal Coll. of Science, London, 1900, and Prof. Watts, Geology, 1901 (Vacation Course). (*Signed by*) Barker North, Robt. D. Abell, T. W. Price.

Sciver, Albert, 84, Vineyard Hill, Wimbledon Park, S.W. 19. English. Analytical and Consulting Chemist and Bacteriologist. B.Sc. (First Class Honours, University College, London), A.I.C. Assistant to Drs. S. and E. K. Rideal, 28, Victoria St., S.W. 1. Lecturer on Bacteriology applied to Chemistry at Battersea Polytechnic. (*Signed by*) F. G. Donnan, Eric K. Rideal, W. E. Garner.

Scott, George Baty, 37, Woodbridge Road, Knowle, Bristol. British. Organic and Inorganic Chemistry Student for two years at Central Polytechnic Institute, after passing the Qualifying Examination of Pharmaceutical Society, 1896. For some years have been closely associated with British Fine Chemicals, embracing Dye Intermediates, Research Chemicals, Saccharin and by-products. Wishful to have access to Society's Library and Publications, thus keeping up to date with the latest advances in Chemistry. (*Signed by*) J. Wicliffe Peck, D. Hughes, T. O. Kent, W. D. Wallace, Archibald Macpherson.

Scammell, Rupert Boswood, c/o F. H. Faulding & Co., Ltd., Castlereagh St., Redfern, Sydney, N.S.W. British. Manufacturing Chemist. Bachelor of Science (Sydney). Six years' experience in Manufacturing Chemistry with the above firm. I desire to keep in touch with modern chemical literature for research purposes. (*Signed by*) J. Kenner, George Harker, J. C. Earl.

Shin, Ufo, B.A.S., Agricultural Farm, Mandalay. Burman. Officiating Agricultural Chemist, Burma, Mandalay. Published as Memoirs of the Department of Agriculture in India on "The Phosphate Requirements of some Lower Burma Paddy Soils." (*Signed by*) Maung Ba, Maung Ba San, Maung Tun Tin.

Singh, Dalip, near Tehsil, P.O. Lahore, India. Indian. Research Student, Cambridge University. Ph.D. Cambridge. (*Signed by*) W. J. Pope, W. H. Mills, Eric K. Rideal.

Smith, Frederick Francis Percival, Peterhouse, Cambridge. British. Research Student in the Cambridge Univ. Laboratories. 1st Class Nat. Sci. Tripos, Parts I and II. 1st Class London Ext. B.Sc. Hons. (in Chemistry). (*Signed by*) Hamilton McCombie, Harold A. Scarborough, W. A. Waters.

Smith, Robert Frederick, 254, Higham Hill Road, Walthamstow, E. 17. British. Student of Chemistry at East London College. Desirous of keeping in touch with Modern Research. (*Signed by*) J. R. Partington, E. E. Turner, Elwyn Roberts.

Soper, William Ernest, 50, Aislibie Road, Lee, London, S.E. 12. British. Research Student at East London College. B.Sc. (Lond.). (*Signed by*) J. R. Partington, E. E. Turner, Elwyn Roberts.

Southern, Herbert Kenneth, Glenariff, Whaley Bridge, Nr. Stockport, Cheshire, also Government Laboratory, Strand, W.C. 2. British. Temporary Assistant Chemist, Government Laboratory. B.Sc. (Hons. Chem.) after 3 years and M.Sc. after a further year's research work in physical chemistry at Manchester University. Assistant Demonstrator in chemistry for 1 year at Manchester University. Six months as chemist with paint and enamel firm; 4 months at Government Laboratory. (*Signed by*) Robert Robertson, J. J. Fox, Geo. Stubbs, T. W. Harrison.

Speight, Eric Alfred, 61, Arthur Road, Wimbledon Park, S.W. 19.

British. Research worker in Organic Chemistry. Associateship of the Royal College of Science. B.Sc. (Lond.), Diploma of Imperial College, all in Chemistry. Have been engaged in study of Chemistry for 6 years, the last two being research. Published paper in Oct. 1924 *J.C.S.* on formation of Hydrindone derivatives. (*Signed by*) Jocelyn Thorpe, G. A. R. Kon, Arnold Stevenson.

Swire, Frank Harland, 152, Queen's Road, Halifax, Yorks. British. Pharmacist. "Minor" Qualification of the Pharmaceutical Society. Member of the Pharmaceutical Society of Gt. Britain. Late Student in Chemistry at the Halifax Technical College and at The School of Pharmacy, Bloomsbury Sq., London, W.C. 1. (*Signed by*) T. E. Wallis, F. Browne, W. J. Stansfield.

Tattersall, Harold James, B.Sc., Ph.D., 141, Thorold Road, Ilford, London, E. British. Research Chemist. Graduate of St. Andrews University. B.Sc., Ph.D. Research work carried out at University College, Dundee. Presently engaged in research photographic chemistry. Publishing under authorship McKenzie and Tattersall, probably in November 1925. (*Signed by*) Alex. McKenzie, O. Rhys Howell, R. Roger, John Foggie.

Thorpe, William Veale, 270, Balham High Road, London, S.W. British. Research Student, Medical Research Council, Mount Vernon, Hampstead, N.W. 3. B.A. (Cambridge Natural Science Tripos, Parts I and II). One year's research at Mount Vernon. (*Signed by*) W. J. Pope, Jocelyn Thorpe, Hamilton McCombie, W. H. Mills.

Towler, William Milburn, 28, Denton Ave., Roundhay, Leeds. British. Student. B.Sc. Hons. Chemistry, Leeds University. (*Signed by*) H. M. Dawson, P. K. Dutt, H. Holness.

Traill, David, 58, Chalmers St., Dunfermline, Scottish. Research Student. B.Sc. (1st Cl. Hons. Chemistry, St. Andrews), 1923. Research in Organic Chemistry, 1923–1925. Macbeth and Traill, *T.*, 1925, **127**, 892; and 1118. (*Signed by*) A. Killen Macbeth, Irvine Masson, James Craik.

Tricker, Elvera Annie, 319, Norwich Rd., Ipswich. British. Student of Chemistry at Bedford College. (*Signed by*) J. F. Spencer, H. Crompton, J. Stewart.

Turner, Donald Morrison, 40–42, Lexington St., W. 1. British. Representative of Mead Johnson & Co., Food Specialists. M.Am.Chem.Soc. Ten years Asst. Analyst, Govt. Laboratory, Newfoundland. Desire to receive the publications of the Society and keep in touch with modern work. (*Signed by*) D. James Davies, G. S. W. Marlow, F. S. Aumonier.

Turner, Geoffrey, 85, Winchester Avenue, Leicester. English. Research Student, attending Loughborough College, Leics. B.Sc. (2nd Class Honours, London); Diploma of Loughborough College (Honours). (*Signed by*) A. Bramley, A. T. Eggington, G. Lawton.

Tyler, Norman Leopold, 9, St. Paul's Gardens, Spennymoor, Co. Durham. British. Chief Chemist and Manager of Messrs. Intermediates and Explosives, Ltd., Dean and Chapter Colliery, Ferryhill, Co. Durham. City and Guilds and South Kensington Examinations, Inorganic and Organic. South Staffs. Scholarship Metallurgy., Iron and Steel. Secretary of N.E. Section of the British Association of Chemists. Fourteen years with Messrs. Chance and Hunt, Ltd., Oldbury and Wednesbury. Chemist in Charge of several plants for eight years. (*Signed by*) S. I. Levy, L. R. B. Pearce, W. A. S. Calder.

Vernon, Herbert Ward, 245, Albert Rd., London, N. 22. British. Research Chemist. B.Sc. in Hons. Chemistry of Victoria University, Manchester. Held post as Research Chemist for last nine years. (*Signed by*) Percy C. C. Isherwood, B. H. Bowles, R. E. Brett.

Webb, Frederick Henry, "St. Malo," Jameson Road, Harpenden. British. Manufacturing Chemist and Optician. (1) Early Education at the Dunstable Grammar School. (2) Studied Analytical Chemistry under J. B. Hoblyn, B.Sc., F.I.C. (3) Studied Chemistry and Physics at the London School of Chemistry under Henry Wootton, B.Sc. (4) Passed the Qualifying Examination of the Pharmaceutical Society in 1910. (5) Passed the Qualifying Examination as a Fellow of the National Association of Opticians in 1923. Particularly interested in Analytical and Scientific work. (*Signed by*) Frank B. Arnold, J. J. Laws, Percy Barrs.

Williams, Ewart Harrod, 31, Thornsbeach Road, Catford, S.E. 6. British. Chemist, Government Laboratory, Clement's Inn Passage, W.C. B.Sc. (Hons. Lond.), A.C.G.F.C., A.I.C. Research work at Finsbury Technical College with Prof. A. J. Hale, and at the Government Laboratory with Dr. J. J. Fox. I desire to keep in touch with modern developments in Pure and Applied Chemistry, through the Society's Journal, and by attending the Scientific Meetings of the Society. (*Signed by*) Robert Robertson, Geo. Stubbs, J. J. Fox, A. G. Francis.

Williams, Gwyn, Cae Ffynnon, Llandudno Junction, North Wales. Welsh. Research Student in Chemistry at University College of North Wales, Bangor. 1924, B.Sc. (Wales) with 1st Class Hons. in Chemistry. 1924–5, Research Student at University College, Bangor. (*Signed by*) Kennedy Orton, F. G. Soper, H. B. Watson.

Williams, Hugh Amphlett, 249, Kennington Rd., S.E. 11. English. Student. Student of the Institute of Chemistry, desiring the use of the Library and the Periodicals. (*Signed by*) George A. Stokes, Ernest W. Wright, A. J. Hale, H. M. Atkinson.

Williams, Robert Harding, 131, Anlaby Road, Hull. British. Chemist (Pharmaceutical), practising as a Chemist at above address. (Leeds University Matric.). Two years at Swansea Municipal College (3rd year Medical Student). M.P.S. (1907). One year Hull Technical College. Was 2 years as Chemist in Middlesbro' (Analytical), and have been in business at above address nearly 4 years. Have been doing analytical work for a number of years. (*Signed by*) Harry Thompson, Thos. A. Nightscales, Edward Chapman.

Wiltshire, John Laurence, 36, Fordel Road, Catford, London, S.E. 6. English. Assistant Works Chemist to Messrs. Burt, Boulton, and Haywood, Coal Tar Distillers, London. B.Sc. London, 2nd Class Honours in Chemistry (1925). Three years' experience with consulting analyst (Mr. F. W. Harbord). Now occupied as above and in pure chemical research under Mr. E. de B. Barnett at the Sir John Cass Technical Institute, London. (*Signed by*) E. de Barry Barnett, Marcus A. Matthews, James W. Cook.

Wolfe, John James Benjamin, 24, Greyhound Road, Hammersmith, W. 6. English. Student (Research), East London College. (*Signed by*) J. R. Partington, Elwyn Roberts, D. C. Jones.

Wright, Gordon Mitchell, University Chemical Labs., Cambridge. British. Research Chemist. M.A. (Cantab.), B.Sc. (Glasgow). (*Signed by*) Hamilton McCombie, A. C. P. Lunn, Harold A. Scarborough.

Wyatt, Wilfred Fisher, North Anston, Nr. Sheffield. British. Demonstrator in Chemistry, the University of Sheffield. B.Sc. Hons. Chemistry, 1923, Sheffield University; M.Sc., 1924, Sheffield University. (*Signed by*) W. P. Wynne, F. G. Tryhorn, G. M. Bennett, Arthur W. Chapman.

Zimmermann, John Frederick, 17, Stile Hall Gardens, Chiswick, W. 4. British. Research Chemist. Diploma of Engineer Chemist, Zurich Poly-

technicum. 2½ Years as Assistant to Dr. Tcherniac. (*Signed by*) J. Tcherniac, A. G. Bloxam, C. S. Gibson.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2).

Cuthbert, Bertram, c/o The British Australian Cotton Assocn., Oil Mills, Brisbane, Australia. British. Oil Mills Manager. 1906–1912, Analytical Chemist, The Hull Oil Manuf. Co., Ltd., Hull, Eng. 1912–1914, Research Chemist, The Hull Oil Manuf. Co., Ltd., Hull, Eng. 1914–1919, Research Chemist and Refinery Manager for the Hull Oil Manuf. Co., Ltd. 1920–1923, Assistant Works Manager and Soap Works Manager for the Hull Oil Manuf. Co., Ltd. 1923 to present time, Oil Mills Manager for the British Aust. Cotton Assocn., Ltd., Brisbane, Queensland, Australia. (*Signed by*) Geo. H. Appleyard, H. W. Potts.

Miller, Edgar Calvin Le Roy, c/o Medical College of Virginia, Richmond, Va., U.S.A. English. Teacher in Medical College of Virginia. Professor of Biological Chemistry and Bacteriology. M.D. (University of Michigan). Secretary of the Virginia Academy of Science. Past secretary and past chairman of the Virginia Section of the American Chemical Society. (*Signed by*) F. P. Dunnington.

Sigot, Albert Louis Auguste, Institut de chimie, 2, Rue Goethe, Strasbourg. Français. Licencié ès Sciences, préparateur à la Faculté des Sciences de l'Université de Strasbourg. Chargé des travaux pratiques de Chimie Physique. (*Signed by*) Louis Hackspill, Georges Baume.

ADDITIONS TO THE LIBRARY.

I. *Donations.*

Abderhalden, Emil. [Editor.] Handbuch der biologischen Arbeitsmethoden. Abt. I. Chemische Methoden, Teil 2, Heft i. Berlin 1925. pp. 456. *M.* 21. (*Recd.* 2/11/25.)
From the Publishers: Herren Urban & Schwarzenburg.

Barbaudy, Jean. Contribution a l'étude de la distillation des mélanges ternaires hétérogènes. Paris 1925. pp. iv + 156. ill. (*Recd.* 11/11/25.) From the Author.

Eucken, Arnold. Fundamentals of physical chemistry. Translated and adapted from the 2nd German edition by Eric R. Jette and Victor K. LaMer. New York 1925. pp. xxiv + 700. ill. 27*s.* 6*d.* net. (*Recd.* 12/11/25.)
From the Publishers: The McGraw-Hill Publishing Co.

Journal of the Chemical Industry. Vol. I, etc. Moscow 1924 +. [In Russian.] (*Reference.*) From Dr. M. Nierenstein.

Kopaczewski, W. Introduction a l'étude des colloïdes: état colloïdal et ses applications. Paris [1925]. pp. viii + 226. ill. 16 *fr.* (*Recd.* 2/11/25.)
From the Publishers: MM. Gauthier-Villars et Cie.

LEVENE, P. A. Hexosamines and mucoproteins. London 1925. pp. x + 164. 10*s*. 6*d*. net. (*Recd*. 22/10/25.)
From the Publishers : Messrs. Longmans, Green & Co.

MASSON, IRVINE. Three centuries of chemistry : phases in the growth of a science. London 1925. pp. 192. ill. 10*s*. 6*d*. net. (*Recd*. 3/11/25.) From the Publishers : Messrs. Ernest Benn.

NAGAOKA, HANTARO. Anniversary volume. By his friends and pupils on the completion of 25 years of his Professorship. Tokyo 1925. pp. xvi + 424. ill. From the Tokyo Imperial University.

RUSSIAN PHYSICAL AND CHEMICAL SOCIETY. Journal. [Chemical Section.] Vol. 55, part 5, etc., Leningrad 1924 +. [In Russian.] (*For circulation*.) From Dr. M. Nierenstein.

THOMS, HERMANN. [Editor.] Handbuch der praktischen und wissenschaftlichen Pharmazie. Vol. III. Part iv. Vol. IV. Part ii. Berlin 1925. pp. [288], [272]. ill. *M*. 20. (*Recd*. 2/11/25.)
From the Publishers : Herren Urban & Schwarzenberg.

WEST, CLARENCE JAY, and BEROLZHEIMER, D.D. Bibliography of bibliographies on chemistry and chemical technology 1900—1924. (Bulletin of the National Research Council, No. 50.) Washington, D.C. 1925. pp. 308. (*Reference*.) $2.50 net.
From the Publishers : The National Research Council.

II. *By Purchase.*

ARNOU, CH. Les industries de la conservation des fruits. 3 parts. Vannes 1925. pp. 356, 280, 142. ill. 55 *fr*. (*Recd*. 5/11/25.)

ARRHENIUS, SVANTE AUGUST. Chemistry in modern life. Translated by CLIFFORD SHATTUCK LEONARD. New York 1925. pp. xvi + 286. ill. 13*s*. 6*d*. net. (*Recd*. 10/11/25.)

DELBRÜCK, MAX. Illustriertes Brauerei-Lexikon. 2nd edition. 2 vols. Edited by F. HAYDUCK. Berlin 1925. pp. iv + 534, ii + 438. ill. (*Reference*.) *M*. 54.

GAMBER, OSWALD. Die Herstellung des Cereisens und die Gewinnung der Chloride der seltenen Erden. Wien 1925. pp. viii + 126. *M*. 4. (*Recd*. 26/10/25.)

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

JAN 21 1926

Informal Lecture, Thursday, November 26th, 1925, at 6 p.m., Dr. N. V. SIDGWICK, M.A., F.R.S., Vice-President, in the Chair.

The CHAIRMAN mentioned that this was the first of the Informal Lectures to be given by the Society, and then called upon Professor R. Robinson, D.Sc., F.R.S., to deliver his Lecture entitled : " Recent Research on the Structural Relationships of some Plant Products."

At the conclusion of the Lecture a Vote of Thanks to the Lecturer was proposed by Professor T. M. Lowry, seconded by Dr. R. H. Pichard, and carried with acclamation, Professor Robinson making due acknowledgment.

Ordinary Scientific Meeting, Thursday, December 3rd, 1925, at 8 p.m., Dr. ARTHUR W. CROSSLEY, C.M.G., C.B.E., LL.D., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows :

	Elected.	Died.
James Kerr Erskine	Dec. 5th, 1889.	April, 1925.
Robert Walter Oddy	May 15th, 1890.	Nov. 24th, 1925.
William Robert Lang	March 4th, 1897.	Nov. 20th, 1925.

Certificates were read for the first time in favour of :

Dattatraya Vishwanath Bal, Rothamsted Experimental Station, Harpenden.
Bernard Meredith Brown, B.Sc., F.I.C., Hill Close, Croham Manor Road, S. Croydon.
Frederick Leslie Clark, 170, Barnsley Road, Sheffield.
Reginald Clifford Fawcett, B.Sc., The Cottage, Pentre, Wrexham.
Ko Ko Gyi, Agricultural College, Mandalay.
Tom Heap, B.Sc., Birch Mount, Church Road, New Mills, Stockport.
Stanley Barker Johnson, c/o Colombo Gas & Water Co., Ltd., Colombo, Ceylon.
Leonard George Jupp, B.Sc., A.R.C.S., 6, Chesham Road, Kemp Town, Brighton.
Horace Alfred Mayes, B.Sc., The Cottage, Sewage Works, Vicarage Lane, East Ham, E. 6.

Henry Geoffrey Ordish, B.A., Chilcombe, Milton Road, Harpenden.
Arnold Piukus, 238, Amhurst Road, Stoke Newington, N. 16.
Clifford Burrough Purves, B.Sc., Edenbank, Cupar.
Suresh Chandra Ray, P.O. Alambazar, Ray Villa, Calcutta.
Edna Clark Smith, B.Sc., 9, Gilston Road, S.W. 10.
Sidney David Sutton, 2, Glasshouse Street, W. 1.
Raymond Taylor, M.A., B.Sc., St. Brelades, Woodside Road, Parkstone.
Richard Victor Thomas, B.A., 17, Pretoria Road, Cambridge.
Henry Wilkins, B.Sc., 13, Kinfauns Road, Goodmayes.
Reginald Frank Wright, A.R.C.S., Fairhazel, Avondale Road, Hove.

Messrs. E. Horton and W. B. Saville were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared elected as Fellows :

Robert Leslie Andrew.
Louis Baissac.
William Francis Barker, Ph.D.
Ralph Basden.
Frank Bell.
Arthur Neville Copnall Bennett, B.Sc.
Harold Frederick Betts, B.Sc.
John Cecil Bird, B.Sc., A.I.C.
Lionel Christopher William Birkett, B.Sc.
James Boyd, F.I.C.
Frank Symonds Bradhurst.
Edward Britnell, B.Sc.
Reginald John Bromfield.
Francis Hereward Burstall, B.Sc.
Archer John William Butterfield.
John Hildred George Carlile, B.Sc., A.R.C.S.
Leslie James Chalk, B.Sc.
Rama Charan, B.Sc., B.Sc.Tech.
John William Corran, B.Sc., Ph.D., A.I.C.
John Harold Cottier.
Edward Mortimer Crowther, D.Sc., F.I.C.
Bertram Cuthbert.
Frank Edwin Dickinson.
Joseph Raymond Dolphin, B.Sc.
William Donovan, M.Sc.
John Stanley Dunn, M.A., Ph.D., A.I.C.
John Horsfall Dyde.
George Malcolm Dyson, B.A., B.Sc., Ph.D.
Alfred Eccles, B.Sc.
Edwin Francis Edwards.
John Moelwyn Edwards.
George Albert Elliott, M.Sc.
Eric Bertram Evans, B.Sc.
Elinor Katharine Ewbank, B.A.
Elizabeth Monica Openshaw Farrow, M.A.
Oliver Free, B.A.
William Marshall Freeman.
Eva Florence Gee.
James Walter Shanks Gemmell, B.Sc.
Francis Reginald Glover.
William Bouch O'Brien Goudielock.
Felix John Theodore Grigg, M.Sc., A.I.C.
George Vincent Hall, B.Sc.
John Hall, M.Sc., A.I.C.
William Rowan Hare.
Walter Healey.
Thomas Henderson, M.C., M.A., B.Sc.
Herbert Sim Hirst.
Syed Husain, M.Sc.
Toru Iwadare.
David Christopher Mendis Jayewardene.
Gilbert Jessop, M.Sc., Ph.D.
Charles Benjamin Johnson.
Walter Idris Jones, B.Sc., Ph.D.
Henry Wilfrid Keenan.
Brian Charles Lavers Kemp, B.A.
Charles King.
Frederick Karl Victor Koch, B.Sc., A.R.C.S.
Charles Dudley Langford, B.Sc., A.R.C.S.
Banarsi Das Laroia, B.A., B.Sc.
Henry Guinness de Laszlo, B.A., Ph.D.
Bertram Grey Leatherbarrow.
Sam Lenher, B.A.
John Joseph Lennon, M.Sc.

William Macartney.
Ivan Roy McHaffie, B.A., M.Sc.
Neil McLean, M.A., B.Sc.
Leslie George Manchester, B.Sc.
William Alfred Nottage Markwell.
William Francis Martin, F.I.C.
Charles Henry Lawrence Miller, B.Sc.
Edgar Calvin le Roy Miller, M.D.
Arthur Moore.
Alexander John Morrison.
Frank Richard Morrison.
John Blackburn Murgatroyd.
Chitsukhlal Hiralal Nanavati.
Henry Nicholson, M.Sc.
Anna Maria O'Meara.
Horace Winston Palmer, B.Sc.
Norman Frederick Parker, B.A., A.I.C.
Austin McDowell Patterson.
Ernest Phillis, B.Sc.
Jonathan Pollitt, B.A.
Charles Raymond Porter, M.Sc., A.I.C.
Evan Emrys Price, B.Sc.
Marjorie Ellen Pring, B.Sc.
Jnanendra Nath Rây, M.Sc.
Herbert Charles Roberts.
Phyllis Mary Sanderson.
Rose Rachel Sass, B.Sc.
Robert Saxon, B.Sc.
Rupert Boswood Scammell, B.Sc.
Albert Sciver, B.Sc., A.I.C.
George Baty Scott.
Upo Shin.
Albert Louis Auguste Sigot.
Dalip Singh, Ph.D.
Frederick Francis Percival Smith, B.A., B.Sc.
Robert Frederick Smith.
William Ernest Soper, B.Sc.
Herbert Kenneth Southern, M.Sc.
Eric Alfred Speight, B.Sc.
Frank Harland Swire.
Harold James Tattersall, B.Sc., Ph.D.
William Veale Thorpe, B.A.
William Milburn Towler, B.Sc.
David, Traill, B.Sc.
Elvera Annie Tricker.
Donald Morrison Turner.
Geoffrey Turner, B.Sc.
Norman Leopold Tyler.
Herbert Ward Vernon, B.Sc.
Frederick Henry Webb.
Ewart Harrod Williams, B.Sc., A.I.C.
Gwyn Williams, B.Sc.
Hugh Amphlett Williams.
Robert Harding Williams.
John Laurence Wiltshire, B.Sc.
John James Benjamin Wolfe.
Gordon Mitchell Wright, M.A., B.Sc.
Wilfred Fisher Wyatt, M.Sc.
John Frederick Zimmermann.

The following papers were read :

"On the Budde effect in bromine. Part I. The photoactive constituent in wet bromine." By B. Lewis and E. K. Rideal.

"On the Budde effect in bromine. Part II. The kinetics of the reaction and the light absorption of wet and dry bromine." By B. Lewis and E. K. Rideal.

"The influence of carbon rings on the velocity of reactions involving their side-chains. Part I. The hydrolysis of cyclic and open-chain malonic esters." By R. Gane and C. K. Ingold.

"The density of boric oxide glass and the suspected variation in the atomic weight of boron." By H. V. A. Briscoe, P. L. Robinson, and G. E. Stephenson.

Ordinary Scientific Meeting, Thursday, December 17th, 1925, at 8 p.m., Dr. Arthur W. Crossley, C.M.G., C.B.E., LL.D., F.R.S., President, in the Chair.

The President referred to the loss sustained by the Society, through death, of the following Fellows:

	Elected.	*Died.*
George Frederick William Blackburn	May 15th, 1913.	Nov. 23rd.
Edmund Knecht	Dec. 1st, 1910.	Dec. 8th.
James Grant	Feb. 6th, 1890	Dec. 7th.

The President announced that:

1. A Special Lecture will be delivered by Professor J. Barcroft, F.R.S., entitled "Hæmoglobin" on Thursday, February 11th, 1926, at 8 p.m. The Lecture will be held in the Chemistry Theatre of the University College, Gower Street, W.C. 1, by the kind permission of the College Authorities.

2. British Chemical Abstracts "A," Pure Chemistry for 1926, printed on one side of the paper only, and gummed or ungummed, will be obtainable by Fellows at the price of £3 0*s.* 0*d.*, post free. Application should be made to the Assistant Secretary, Mr. S. E. Carr, as soon as possible.

The following were formally admitted Fellows of the Chemical Society: Thomas M. Sharp, Arthur Moor, Cecil J. May, J. F. Zimmermann, F. Bell, C. D. Langford,and J. M. Edwards.

Certificates were read for the first time in favour of:

Edwin Melhuish Bailey, Almond Hill, Pumpherston, Midcalder.
Carl Howard Collie, B.A., New College, Oxford.
William Eric Downey, Ph.D., Imperial College of Science and Technology, S. Kensington, S.W. 7.
Andor Fodor, Ph.D., Hebrew University, Jerusalem.
Herbert Harris, B.Sc., Ph.D., A.R.C.S., 1, Royal York Villas, Clifton, Bristol.
Ralph Harry Klein, A.I.C., 11, Park Place Villas, Maida Hill, W. 2.
Montague Alexander Phillips, A.I.C., 31, Cator Street, S.E. 15.
Devasikhamani Sunderavelu Pillai, 37, Hill Street, Stoke-on-Trent.
Charles Aylmore Ray, B.A., 47, Somerford Grove, Tottenham, N. 17.
Ivy Winifred Elizabeth Rogers, 8, St. Lawrence Road, W. 10.
Ronald Stanley Russell, B.A., 47, Redington Road, Hampstead, N.W. 3.
Robert John Schaffer, B.A., B.Sc., 3, Hambalt Road, S.W. 4.
Charles Richard Noël Strouts, B.A., B.Sc., A.I.C., Westminster Bank, Kew Gardens, Surrey.
Frank Sherwood Taylor, M.A., B.Sc., 21, Shortlands Road, Shortlands, Kent.
Claude Stanley Watson-Will, Musgrave Road, Indooroopilly, Brisbane.
Idris Williams, B.A., 19, Silver Street, Cambridge.

The meeting was then adjourned, and the Informal Meeting declared open.

The Council has made the following Grants from the Research Fund :

	£	s.	d.
Preparation and investigation of rare earth carbides. N. L. Anfilogoff	10	0	0
Preparation of phenanthrenes from stilbenes. J. N. Ashley ...	5	0	0
Investigation of certain binary and ternary systems. C. R. Bailey	5	0	0
Synthesis of genistein. W. Baker	15	0	0
Studies in the anthracene series (*contd.*). E. de B. Barnett ...	5	0	0
(*a*) Studies in aliphatic and cyclic sulphides			
(*b*) Reactivity of some quinoxaline bases. G. M. Bennett ...	5	0	0
Study of the mutual solubility relations of certain binary liquid systems. H. F. Betts	3	0	0
The dynamic isomerism of menthyl–cotarnine and of assymmetrical xanthydrols. B. C. Chatterjee	12	0	0
Thiocyano- and selenocyano-groups in the aromatic nucleus. F. Challenger	5	0	0
Preparation and study of certain polyhydroxy derivatives of diphenic acid. G. H. Christie	5	0	0
Synthesis of substituted tri- and tetra-methylene ring derivatives from compounds obtained by condensation of malonic ester with aldehydes. H. Clayton	5	0	0
Anthranyl ketones. J. W. Cook	5	0	0
Addition of bivalent carbon compounds to bodies of the diazomethane class. K. Cooper	5	0	0
Stability of Schiff's bases. P. K. Dutt	5	0	0
Conversion of asymmetric bromo compounds into the corresponding sulphonic acids. E. B. Evans	5	0	0
Influence of the benzoyl group on the mobility of the three-carbon tautomeric system. M. D. Farrow	10	0	0
Studies in the catalytic activity of charcoal. J. B. Firth ...	10	0	0
Solubility relationships of alums and pseudo alums. S. Glasstone	3	0	0
Study of alkylene thiosulphates and of alkylene disulphonic acids. J. Goodspeed	5	0	0
Quasi-aromatic structure (*contd.*). F. R. Goss	5	0	0
Properties of conjugated compounds. A. T. Healey	6	0	0
Periodic chemical reactions. E. S. Hedges	15	0	0
Substitution in the aromatic nucleus. W. J. Hickinbottom ...	4	0	0
Photochemical combination of hydrogen with other gases. H. S. Hirst	7	0	0
(*a*) Synthetical experiments in the anthocyanidin series ...			
(*b*) Synthesis of indole derivatives. H. R. Ing	10	0	0
Conditions of equilibrium between alkali and alkaline earth halides and the alcohols (*contd.*). W. J. Jones	8	0	0
The chemistry of the three-carbon system. L. G. Jupp ...	8	0	0
(*a*) Reaction with ammonia of various unsaturated cyano esters			
(*b*) Methylation and ethylation products of various unsaturated cyano amides. (Miss) W. Kilroy	5	0	0
Lactone formation from the $\alpha\alpha'$- $\beta\beta'$-dibromo adipic acids. C. D. Langford	6	0	0
Properties of conjugated compounds. B. D. Laroia	6	0	0
Substituted diphenyl compounds. R. J. W. Le Fèvre	5	0	0

	£	s.	d.
Condition of formation and stability of carbon rings. J. J. Lennon	8	0	0
Action of nitric acid on unsaturated hydrocarbons. (Miss) P. V. McKie	10	0	0
Synthesis of (*a*) Degradation product of brucine, and (*b*) Harmaline and some of its derivatives. R. H. F. Manske ...	10	0	0
The effect of bulky groups on the mobility of the 3-carbon system. C. J. May	5	0	0
Researches on thallium compounds (*contd.*). R. C. Menzies ...	8	0	0
Three carbon tautomerism. B. T. Narayanan	6	0	0
Kinetics of the induction period of the hydrogen-chlorine reaction with ultra-violet light. R. G. W. Norrish	10	0	0
Action of ozone on dry iodine. H. W. Palmer	5	0	0
Nitration of substituted phthalides. J. N. Rây	7	0	0
Reactions between 1 : 3-diketones and amino and amido bodies. E. Roberts	5	0	0
Investigation of certain sesquiterpenes. J. M. Robertson ...	5	0	0
Properties of unsaturated cyclic ketones. J. Ross	5	0	0
The direct introduction of substituents into a mono-substituted diphenyl. H. A. Scarborough	5	0	0
Preparation and properties of various types of halogenated naphthalene derivatives. J. B. Shoesmith	10	0	0
Researches on sulphuryl chloride and chlorination. O. Silberrad	5	0	0
Influence of substituents on the stability of certain spiro and associated ring systems. S. S. G. Sircar	6	0	0
The basic salts, salts of mixed acids, and complex salts of metals of the 3rd and 8th periodic groups. J. D. Main Smith ...	12	0	0
Nitration studies of tertiary aromatic amines. J. M. Smith ...	5	0	0
Condensation reactions with certain β-halogenated acids. M. G. Thomson	5	0	0
Introduction of the methylene-dioxy group and of similar groups into the aromatic nucleus. V. M. Trikojus	8	0	0
Conversion of substituted aromatic amines into quinolines. E. E. Turner	5	0	0
Effect of polar substituents on the Walden inversion among benzene derivatives. E. E. Turner	5	0	0
The chemistry of molybdenum. W. Wardlaw	5	0	0
Reaction of halogens with aliphatic acids, anhydrides, and allied substances. H. B. Watson	5	0	0
(*a*) Spatial structure of *cyclo*paraffins			
(*b*) Constitution of the mono-chloro- and mono-bromo-methyl succinic acids. W. A. Wightman	5	0	0
(*a*) The migratory aptitudes of methoxy-phenyl groups			
(*b*) Experiments upon phthalophenone derivatives, etc. E. W. Wignall	10	0	0
Structural mobility in dihydromuconic systems. R. F. Wright .	5	0	0
Total	£388	0	0

List of papers, or abstracts thereof, received between November 20th and December 17th, 1925. (This list does not include titles of papers which have been read at an Ordinary Scientific Meeting, or which have appeared in the Journal.)

"The mechanism of the formation of *o*- and *m*-hydroxybenzaldehydes from the nitration product of benzaldehyde." By H. H. Hodgson and H. G. Beard.

"The constitution of the normal monosaccharides. Part III. Rhamnose." By E. L. Hirst and A. K. Macbeth.

"Resolution of *dl*-dicentrine." By R. D. Haworth, W. H. Perkin, and J. Rankin.

"Synthetical experiments in the *iso*quinoline group. Part VI. A synthesis of derivatives of paraberine." By R. Campbell, R. D. Haworth, and W. H. Perkin.

"The action of alkaline arsenites on some halogenated organic compounds." By I. E. Balaban.

"The equivalent conductivity of solutions of sodium hydroxide and the mobility of the hydroxyl ion." By H. R. Raikes, A. F. Yorke, and F. K. Ewart.

"An investigation of the zirconium in Colorado pitchblende." By O. Free.

"Some products from the resins of *Xanthorrhœa, Hastilis, X. Arborea*, and *X. Reflexa*." By H.H. Finlayson.

"The nitration of β-naphthoic acid and some new amino- and nitronaphthoic acids." By H. A. Harrison and F. A. Royle.

"Preparation of *p*-bromophenylhydroxylamine by the emulsification process. A modification." By R. D. Haworth and A. Lapworth.

"Optical activity and the polarity of substituent groups. Part III. Menthyl acetophenone-*o*-carboxylate." By H. G. Rule and J. Smith.

"The crystal structure of catechol." By W. A. Caspari.

"The chlorination and bromination of 4-aminodiphenyl." By H. A. Scarborough and W. A. Waters.

"Studies of dynamic isomerism. Part XXI. The velocity of mutarotation of glucose and of tetramethylglucose in aqueous alcohols." By E. M. Richards and T. M. Lowry.

"Studies of dynamic isomerism. Part XXII. The velocity of mutarotation of glucose and of tetra-acetylglucose in aqueous acetone." By G. G. Jones and T. M. Lowry.

"Some unsymmetrically substituted dinitro and diamino derivatives in the stilbene and tolane series. Part I. The fission of hydrogen chloride from 3 : 4′-dinitrostilbene dichloride." By H. A. Harrison and H. Wood.

"The mercuration of aromatic substances. Part II. Orthonitrotoluene." By S. Coffey.

"*N*-Alkylated amidines." By M. Sen and J. N. Ray.

"The equilibrium between ethyl alcohol and the alkali and alkaline earth salts. Part I." By D. G. R. Bonnell and W. J. Jones.

"The dissociation pressures of alcoholates. Part I." By D. G. R. Bonnell and W. J. Jones.

"Ethyl hydrogen sulphate. Part II." By M. A. Hamid, K. Singh, and H. B. Dunnicliff.

"Heterogeneous equilibria between the sulphates and nitrates of sodium and potassium and their aqueous solutions. Part I. The ternary systems." By M. A. Hamid.

"Heterogeneous equilibria between the sulphates and nitrates of sodium and potassium and their aqueous solutions. Part II. The quaternary system H_2O–Na_2SO_4–$NaNO_3$–K_2SO_4–KNO_3." By M. A. Hamid.

"A new reaction of certain diazosulphonates derived from β-naphthol-1-sulphonic acid. Part I. The preparation of phthalazine, phthalazone, and phthalimidine derivatives from 4′-nitrobenzene-2-naphthol-1-diazosulphonate." By F. M. Rowe, E. Levin, A. C. Burns, J. S. H. Davies, and W. Tepper.

"Substituted dihydropentazines—a new series of cyclic nitrogen compounds." By F. D. Chattaway and G. D. Parkes.

"Dvi-manganese." By J. G. F. Druce and F. H. Loring.

"Preparation, hydrolysis, and reduction of the fluoro-, chloro-, and bromo-benzyl bromides." By J. B. Shoesmith and R. H. Slater.

"Absorption spectra of condensed nuclear hydrocarbons." By N. S. Capper and J. K. Marsh.

"The melting points of the normal saturated dibasic acids." By D. A. Fairweather.

"Tautomerism in the thyroxin molecule." By C. S. Hicks.

"The structure of the normal monosaccharides. Part IV. Glucose." By E. L. Hirst.

"An investigation of the hydrated fluoride of zirconium and the preparation of a hydrofluozirconic acid." By E. B. R. Prideaux and E. C. Roper.

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